Catalytic Asymmetric Hydrosilylation of Olefins and Ketones(Dissertation_全文)

AUTHOR(S):

Hayashi, Tamio

CATALYTIC ASYMMETRIC HYDROSILYLATION OF OLEFINS AND KETONES

TAMIO HAYASHI

CATALYTIC ASYMMETRIC HYDROSILYLATION OF OLEFINS AND KETONES

A thesis presented

by

Tamio Hayashi

1975

Department of Synthetic Chemistry

Kyoto University

PREFACE

The studies presented in this thesis have been carried out under the direction of Prof. Makoto Kumada at the Department of Synthetic Chemistry of Kyoto University during 1970-1975. The thesis is concerned with asymmetric hydrosilylation of olefins and ketones catalyzed by platinum, nickel, and rhodium complexes with chiral phosphines as ligands.

The author wishes to express his sincerest thanks to Prof. Makoto Kumada for his kind guidance and helpful suggestions throughout the course of the study. He is also deeply grateful to Dr. Keiji Yamamoto for his continuing guidance and valuable discussions. He wishes to acknowledge the suggestions and criticisms of Assistant Prof. Mitsuo Ishikawa and Dr. Kohei Tamao. Furthermore, the author is also indebted to Messrs. Ryuichi Ito, Yoshihito Uramoto, Michio Zembayashi, Fumio Sakurai, and Hiroshi Omizu for their active collaborations, and to the other members of the research group of Prof. Makoto Kumada for their great kindness and friendly goodwills in carring out the laboratory works.

Finally, the author is grateful to his wife and parents for their constant assistance and encouragement.

Tamio Hayashi

February 1975

CONTENTS

General Introduction

1. Background of the catalytic asymmetric hydrosilylation

Asymmetric synthesis. Asymmetric synthesis refers to a process in which a *prochiral* unit in molecules is converted into a *chiral* unit under certain chiral influences, which arise generally from chiral centers present in either a reagent or a substrate, in such a way that the resulting pair of stereoisomers is formed in unequal amounts.[1] Reaction of a chiral reagent with one or the other of two *enantiotopic* groups or faces (prochiral substrates) under kinetically controlled conditions leads to different diastereomeric transition states. This is the reason why the reaction produces unequal amounts of the stereoisomeric products. The process, therefore, has attracted much interest in realizing the formation of optically active substances from both practical and theoretical points of view.

The asymmetric synthesis falls, at least formally, into two classes, *i.e.* a stoichiometric chemical reaction and a catalytic one with either homogeneous or heterogeneous catalyst. Most of the conventional asymmetric reactions have been carried out using a stoichiometric amount of an optically active reagent,[1c] while catalytic asymmetric reactions require ideally only one molecule of a chiral catalyst in order to produce a large quantity of optically active substances.[1e] Hence, the process would be the most effective one as far as a high optical purity of the product be guaranteed.

The particular terminology presented here *in italic* is based on the Mislow's review: K. Mislow and M. Raban, 'Stereoisomeric Relationships of Groups in Molecules' in "Topics in Stereochemistry", Ed., N. L. Allinger and E. L. Eliel, Interscience (1967) Vol. 1.

Homogeneous catalysis. The mechanisms of homogeneously catalyzed reactions have been of considerable interest for a number of reasons.[2] A large body of data accumulated is especially for the homogeneous hydrogenation of unsaturated molecules, which allows the formulation of empirical rules for the selection of a catalyst.[2c]

Izumi and his coworkers[3] have been reporting their pioneering work on the related field using heterogeneous catalysts such as palladium on silk or Raney nickel modified with naturally occurring acids. However, the difficulty inherent in characterizing the catalyst species renders the task of explaining the existing data in terms of a mechanistic rationale very formidable. Thus the studies on homogeneous catalysis may offer the attractive possibility of characterizing the exact nature of the catalyst precursor,[4] and the steric and electronic factors which exist throughout the reaction path. Having this type of information, it may be possible to design catalytic systems for asymmetric syntheses.

Although a few studies had preceded to realize the homogeneously catalyzed asymmetric reaction, it was not until 1968 that a stereoselective reduction of prochiral olefins inducing some extent of optical activity in the product was reported to be catalyzed by a rhodium complex with chiral phosphine ligands.[2c,5] Since then, studies on homogeneous asymmetric hydrogenation of olefins have appeared in full blast, some of them achieving remarkable results.[6]

The attractive approach to this subject was made possible mainly by the development of route to prepare optically active phosphines.[7] Yet, one of the crucial problems in studies on the catalytic asymmetric synthesis is how to develop a chiral ligand which will enable the catalyst for a given reaction to be as efficient in stereoselectivity as possible. At the present time the choice of the chiral ligand for this purpose is quite

empirical.

Knowles *et al.*[8] and Kagan and coworkers[9] have found that the catalytic hydrogenation of α-acylamidocinnamic acids affords the corresponding amino acid derivatives with 80-90% enantiomeric purity using rhodium complexed with (*R*)-*o*-anisylcyclohexylmethylphosphine and (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane (DIOP), respectively.

What has turned out to be an attractive approach to the asymmetric synthesis is not restricted to the hydrogenation. In fact, it has applied to date to most of cases where the catalytic reaction uses an unsaturated substrate: they are hydroformylation,[10] dimerization or oligomerization,[11] cyclopropanation,[12] and hydrosilylation,[1e,13] the last being the subject of the present thesis.

Hydrosilylation. The addition of hydrosilanes to carbon-carbon multiple bonds (known as hydrosilylation) is catalyzed by a variety of Group VIII transition metal complexes, and is one of the most important laboratory, and also industrial, methods for the preparation of organosilicon compounds.[14]

A mechanism for the platinum(II) complex-catalyzed hydrosilylation has been proposed by Chalk and Harrod[15] in terms of "coordination catalysis", which is now widely accepted for other catalyst systems than the platinum.

In addition, a few points of interest with respect to a stereochemical course of the reaction have already been elucidated. (1) Although the reaction is frequently accompanied by some isomerization of olefins employed, the addition product is thermally stable under usual conditions. This is exemplified by the fact that optically active 2-methylbutyltrichlorosilane does not suffer any racemization,[16] which means no re-elimination of a hydrosilane from the addition product; (2) an oxidative addition of (+)-α-naphthylphenylmethylsilane to platinum(II) complexes takes place with almost complete retention of configuration.[17] The

resulting hydridometal moiety adds across the carbon-carbon double bond of coordinated olefin in a *cis* fashion which is well established; and (3) a reductive elimination step to form the final addition product is most likely to proceed with retention of configuration at both silicon and carbon atoms *via* quasi-cyclic mechanism (S_N^i-Si).[18]

These facts seem to be indispensable for undertaking the asymmetric hydrosilylation of certain of unsaturated compounds.

2. Survey of the present studies

The present thesis composed of nine chapters deals mainly with asymmetric hydrosilylation of olefins and ketones catalyzed by certain of platinum, nickel, and rhodium complexes with chiral phosphines as ligands.

In Chapter 1, the author has described the hydrosilylation of olefins using a few phosphine-platinum(0) complexes. Despite ample instances to show a high efficiency of chloroplatinic acid as a catalyst for hydrosilylation, little attention has as yet been paid to the catalytic activity of platinum complexes containing tertiary phosphines as ligands. It has been disclosed that the phosphine-platinum(0) complexes do catalyze the hydrosilylation of terminal olefins under mild conditions, and that some silyl-platinum(II) complexes can be isolated from the resulting reaction mixture. This study has enabled us to lose no time in undertaking an investigation on asymmetric hydrosilylation of olefins using chiral phosphine-platinum complexes.

Chapter 2 describes the chiral phosphine-platinum(II) complexes as hydrosilylation catalysts. Asymmetric hydrosilylation has been realized for the first time in the reaction of methyldichlorosilane with 1,1-disubstituted olefins such as α-methylstyrene using a platinum complex of the type $[L^*PtCl_2]_2$, where L* is (*R*)-benzylmethylphenylphosphine (BMPP) or (*R*)-methylphenyl-*n*-propylphosphine (MPPP) (eq. 1), though the optical yields

$$RMeC{=}CH_2 + HSiMeCl_2 \xrightarrow{[L^*PtCl_2]_2} RMe\overset{*}{C}HCH_2SiMeCl_2 \qquad (1)$$

obtained are considerably low.

Chapters 3 and 4 are concerned with the asymmetric hydrosilylation of prochiral olefins catalyzed by chiral phosphine-nickel(II) and -rhodium(I) complexes, respectively. A nickel(II) complex of BMPP was found to catalyze the hydrosilylation in higher optical yield than the platinum(II) system. The stereochemical course to differentiate one *enantiotopic* face in the olefin from another is discussed in terms of mechanisms proposed for transition metal-catalyzed hydrosilylation. Evidence is presented for a minor effect of the change in structure of hydrosilanes on the stereoselectivity in the reaction by the use of a rhodium catalyst.

In connection with these studies, the author took a growing interest in asymmetric hydrosilylation of carbonyl compounds. In contrast to a number of studies on the catalytic hydrogenation and hydrosilylation of carbon-carbon multiple bonds, there had been few papers to indicate definite evidence for activation of ketone carbonyls by transition metal complexes, when he began to investigate the catalytic hydrosilylation of ketones, which the following three chapters concern.

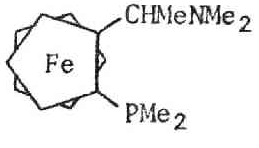
In Chapter 5 is described a brief survey of catalysis in the ketone hydrosilylation and the asymmetric hydrosilylation of a variety of ketones catalyzed by chiral phosphine-platinum(II) complexes. $[(PhMe_2P)PtCl_2]_2$ has been found to be the most effective catalyst for the hydrosilylation of simple ketones so far as methyldichlorosilane is used. Asymmetric hydrosilylation of a series of alkyl phenyl ketones in the presence of $[L^*PtCl_2]_2$, L* = BMPP or MPPP, gives the corresponding silyl

ethers of partially active 1-phenylalkanols. Since the silyl ethers are readily converted into the alcohols, the hydrosilylation of carbonyl compounds may be considered as a synthetically equivalent means to reduction (eq. 2).

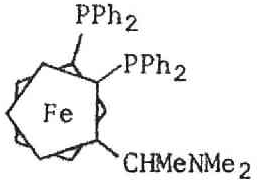
$$R^1COR^2 + HSiR_3 \xrightarrow{\text{chiral cat.}} R^1R^2\overset{*}{C}HOSiR_3 \xrightarrow{H_3O^+} R^1R^2\overset{*}{C}HOH \qquad (2)$$

Rhodium complexes with BMPP or DIOP as ligands are found later to be much more highly selective catalyst than the platinum(II) system, and, in addition, various kinds of trialkyl and dialkylsilanes can successfully be used. These are presented in great detail in Chapter 6. The extent of asymmetric induction is dependent markedly on the structure of hydrosilanes as well as that of ketones employed, and considerably high optical yields (up to 61.8%) are attained by a match of steric needs for these reactants. On the basis of accumulated data, a mechanism involving the formation of diastereomeric α-siloxyalkyl-rhodium intermediates is proposed for the asymmetric hydrosilylation of ketones.

Chapter 7 deals with the preparation of several chiral ferrocenylphosphines having a planar element of chirality, and their novel properties as ligands of a rhodium catalyst for the asymmetric hydrosilylation of ketones. Rhodium complexes with (*R*)-α-[(*S*)-2-dimethylphosphinoferrocenyl]ethyldimethylamine (MPFA)



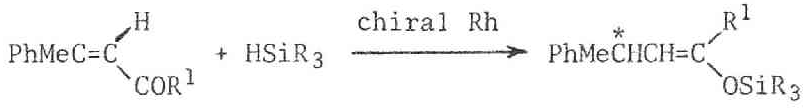
(*R*)-(*S*)-MPFA



(*S*)-(*R*)-BPPFA

or (*S*)-α-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]ethyldimethyl amine (BPPFA) are proved to catalyze the reaction as efficiently with respect to stereoselectivity as those with chiral phosphine ligands mentioned above.

As a necessary extention Chapter 8 is concerned with the asymmetric hydrosilylation of α,β-unsatureated ketones and aldehydes, the latter being found to be of no use for asymmetric induction. The observed 1,4-addition provides a facile route to the preparation of optically active silyl enol ethers (eq. 3).



(3)

The fact that an oxidative addition of (+)-α-naphthylphenylmethylsilane to a suitable complex takes place with retention of configuration (*vide supra*) allows one to expect a possibility to induce asymmetry at a *meso* silicon atom of the type $H_2SiR^1R^2$. This is substantiated by means of asymmetric addition of prochiral diorganosilanes to symmetrically substituted ketones. In Chapter 9, the author has applied the catalytic asymmetric hydrosilylation of ketones catalyzed by chiral rhodium complexes to the preparation of some new optically active bifunctional organosilanes associated with an asymmetry at the silicon atom (eq. 4). The reaction becomes a first example of asymmetric induction around the silicon atom.

(4)

REFERENCES

1. For pertinent books and reviews: (a) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill (1962); (b) K. Mislow, "Introduction to Stereochemistry", Benjamin (1965); (c) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall (1971); (d) T. D. Inch, Synthesis, 2, 466 (1970); (e) K. Yamamoto, Kagaku To Kogyo, 26, 193 (1973); (f) J. W. Scott and D. Valentine, Jr., Science, 184, 943 (1974); (g) L. Marko and B. Heil, Cat. Revs., 8, 269 (1973).
2. (a) G. N. Schrauzer, Ed., "Transition Metals in Homogeneous Catalysis", Marcel Dekker (1972); (b) B. R. James, "Homogeneous Hydrogenation", Wiley (1972); (c) R. E. Harmon, S. K. Gupta, and D. J. Brown, Chem. Revs., 73, 35 (1973).
3. Y. Izumi, Angew. Chem., 83, 956 (1971), and his previous papers cited therein.
4. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Ed., Interscience (1972), Chapt. 24.
5. (a) L. Horner, H. Siegel, and H. Büthe, Angew. Chem., 80, 1034 (1968); L. Horner and H. Siegel, Phosphorus, 1, 209 (1972); (b) W. S. Knowles and M. J. Sabacky, Chem. Commun., 1445 (1968).
6. (a) P. Abley and F. J. McQuillin, Chem. Commun., 477 (1969); idem, J. Chem. Soc.,C, 844 (1971); (b) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, J. Amer. Chem. Soc., 93, 1301 (1971).
7. K. Naumann, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 91, 7012 (1969), and references cited therein.
8. W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, J. C. S. Chem. Commun., 10 (1972).
9. T.-P. Dang and H. B. Kagan, Chem. Commun., 481 (1971); idem, J. Amer. Chem. Soc., 94, 6429 (1972).
10. (a) C. Botteghi, G. Consiglio, and P. Pino, Chimia, 26, 141

(1972); G. Consiglio, C. Botteghi, C. Salomon, and P. Pino, Angew. Chem., 85, 663 (1973); (b) C. Botteghi, G. Consiglio, and P. Pino, Chimia, 27, 477 (1973); (c) I. Ogata and Y. Ikeda, Chem. Lett., 487 (1972); (d) M. Tanaka, Y. Watanabe, T. Mitsudo, K. Yamamoto, and Y. Takegami, Chem. Lett., 483 (1972); (e) B. Stern, A. Hirschauer, and L. Sajus, Tetrahedron Lett., 3247 (1973).

11. (a) B. Bogdanovic, B. Henc, B. Meister, H. Pauling, and G. Wilke, Angew. Chem., 84, 1070 (1972); B. Bogdanovic, Angew. Chem., 85, 1013 (1973), and their previous papers therein.
12. (a) H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, Tetrahedron, 24, 3655 (1968); (b) R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, Can. J. Chem., 47, 1242 (1969); (c) S. Otsuka, A. Nakamura, A. Konishi, and Y. Tatsuno, Symposium on Organometallic Chemistry, Kyoto, Japan, 1974; Abstr., pp 110.
13. For a review: I. Ojima, Yuki Gosei Kagaku Kyokai Shi, 32, 687 (1974).
14. (a) C. Eaborn and B. W. Bott in A. G. MacDiarmid, Ed., "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, Marcel Dekker (1968), p 231-263; (b) E. Ya. Lukevits and M. G. Voronkov, "Organic Insertion Reaction of Group IV Elements", Consultants Bureau (1966).
15. A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 87, 16 (1965).
16. L. Spialter and D. H. O'Brien, J. Org. Chem., 31, 3048 (1966).
17. C. Eaborn, D. J. Tune, and D. R. M. Walton, J. Chem. Soc. Dalton, 2255 (1973)
18. L. H. Sommer, L. E. Lyons, and H. Fujimoto, J. Amer. Chem. Soc., 91, 7051 (1969).

Chapter 1

Interaction of Silanes with Bis(triphenylphosphine)ethylene-platinum(0); Hydrosilylation of Olefins with This Complex[1]

SUMMARY

Bis(triphenylphosphine)ethyleneplatinum(0) ($PtL_2(C_2H_4)$) and two other triphenylphosphine-platinum(0) complexes (PtL_3 and PtL_4) were found to be effective catalysts for hydrosilylation of terminal olefins. Two types of silylplatinum(II) complexes depending on the hydrosilanes used were isolated from the reaction mixture. $PtL_2(C_2H_4)$ also catalyzes the addition of methyldichlorosilane to butadiene and isoprene in a 1,2-fashion, quite unlike the palladium or nickel complex-catalyzed 1,4-addition.

INTRODUCTION

The catalytic addition reaction of silicon hydrides to various kinds of olefins and acetylenes has become one of the most important laboratory methods of forming a silicon-carbon bond known as hydrosilylation.[2] Chloroplatinic acid is by far the most commonly used catalyst for the reaction.[3,4] Recently, it has been shown that tertiary phosphine-metal complexes of palladium,[5,6] nickel,[5,7,8] and rhodium[9,10] are also effective as catalysts, exhibiting individual catalytic characteristics. However, there have been few reports to indicate a definite catalytic activity of platinum complexes with phosphine ligands for the hydrosilylation.

In this connection, it is of considerable interest that *trans*-dichlorobis(triethylphosphine)platinum(II) and tributylphosphine analog[11] do catalyze the hydrosilylation of terminal olefins.[12] In addition, current interest in a facile oxidative addition of simple molecules to $PtL_2(C_2H_4)$[13] (L = PPh_3) prompted us to investigate the reaction of this complex with hydrosilanes, as well as its effectiveness as hydrosilylation catalyst.

In this chapter, we describe the scope of hydrosilylation catalyzed by phosphine-platinum(0) complexes and the first examples of isolation of some silyl-platinum(II) complexes formed in the course of hydrosilylation.

After our preliminary report[1] had been published, exactly the same subject of research as ours was reported independently by Fink *et al.*.[14]

RESULTS AND DISCUSSION

Bis(triphenylphosphine)ethyleneplatinum(0),[13] $PtL_2(C_2H_4)$ (L = PPh_3), catalyzed the addition reaction of various hydrosilanes to terminal olefins such as 1-hexene to afford terminal adducts in almost quantitative yield (eq. 1). PtL_3 and PtL_4 were also found to be active catalysts.

$$RCH{=}CH_2 \;+\; HSiR'_3 \xrightarrow[90^\circ]{[Pt(0)]} RCH_2CH_2SiR'_3 \qquad (1)$$

R = *n*-C_4H_9, *n*-C_6H_{13}, Me_2EtSi

$HSiR'_3$ = $HSiCl_3$, $HSiMeCl_2$, $HSiMe_2Cl$, $HSiMe_3$, $HSiMe_2Et$, $HSiMe(OEt)_2$, $HSiPhCl_2$

[Pt(0)] = $PtL_2(C_2H_4)$, PtL_3, PtL_4

Table I. Hydrosilylation of Olefi s Catalyzed by Plati.um(0) Complexes.[a]

Olefin	Silane	Catalyst	Product	Yield (%)
n-$C_4H_9CH=CH_2$	$HSiMeCl_2$	PtL_4	n-$C_6H_{13}SiMeCl_2$	[b]
n-$C_4H_9CH=CH_2$	$HSiMeCl_2$	PtL_3	n-$C_6H_{13}SiMeCl_2$	[b]
n-$C_4H_9CH=CH_2$	$HSiMeCl_2$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiMeCl_2$	[b]
n-$C_4H_9CH=CH_2$	$HSiCl_3$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiCl_3$	[b]
n-$C_4H_9CH=CH_2$	$HSiMe_2Cl$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiMe_2Cl$	[b]
n-$C_4H_9CH=CH_2$	$HSiMe_3$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiMe_3$	[b]
n-$C_4H_9CH=CH_2$	$HSiMe_2Et$	PtL_3	n-$C_6H_{13}SiMe_2Et$	[b]
n-$C_4H_9CH=CH_2$	$HSiMe(OEt)_2$	PtL_3	n-$C_6H_{13}SiMe(OEt)_2$	95
n-$C_4H_9CH=CH_2$	$HSiPhCl_2$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiPhCl_2$	90
n-$C_6H_{13}CH=CH_2$	$HSiMeCl_2$	PtL_3	n-$C_8H_{17}SiMeCl_2$	[b]
$Me_2EtSiCH=CH_2$	$HSiMeCl_2$	PtL_3	$Me_2EtSiCH_2CH_2$-$SiMeCl_2$	[b]
n-$C_3H_7CH=CHCH_3$	$HSiMeCl_2$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiMeCl_2$	< 5
n-$C_3H_7CH=CHCH_3$	$HSiMeCl_2$	$PtL_2(C_2H_4)$	n-$C_6H_{13}SiMeCl_2$	60[c]
n-$C_3H_7CH=CHCH_3$	$HSiMe_2Et$	PtL_3	n-$C_6H_{13}SiMe_2Et$	< 5
Cyclohexene	$HSiMeCl_2$	$PtL_2(C_2H_4)$	—	0[c]
1,5-Cyclo-octadiene	$HSiMeCl_2$	PtL_3	—	0

[a] The reaction was carried out at 90° for 11 hr unless otherwise noted. [b] Quantitative yield. [c] Heated at 140°.

The platinum(0) complexes did not catalyze the reaction of internal olefins such as 2-hexene and cycloolefins at 90°. At elevated temperature (140°), the reaction of 2-hexene with methyldichlorosilane could occur to give n-hexylmethyldichlorosilane in a low yield. These results obtained are summarized in Table I. There seems no appreciable difference in the catalytic characteristics between platinum(0) complexes and conventional chloro-

platinic acid, though the latter is assumed to be active in a low oxidation state as a result of initial reduction by the hydrosilane.[4]

Using a sufficient amount of $PtL_2(C_2H_4)$, the isolation of a platinum complex was undertaken. From a reaction mixture of $PtL_2(C_2H_4)$, 1-hexene, and methyldichlorosilane were obtained fine white crystals (in 70% yield), which were characterized as *cis*-hydridomethyldichlorosilylbis(triphenylphosphine)platinum(II) (1), ir(KBr): 2110 cm^{-1} (ν(Pt-H)), 1240 cm^{-1} (δ(Si-CH_3)), 790 and 750 cm^{-1} (δ(Pt-H)/δ(Si-CH_3)), and 450 cm^{-1} (ν(Pt-P), doublet). This hydridosilylplatinum complex (1) was too insoluble for its configuration to be assigned beyond doubt by nmr. 1 has been also prepared by Fink *et al.*[14b] by treatment of PtL_4 with methyldichlorosilane in hexane or 1-hexene at 25-30°. A little later, Eaborn and coworkers[15] reported that in the absence of a solvent various hydrosilanes including triarylsilanes are able to add to $PtL_2(C_2H_4)$ in the mode of an oxidative elimination to give the hydridosilylplatinum complexes.

Under our conditions but without 1-hexene, another silylplatinum complex was obtained and this was identified to be *cis*-bis(methyldichlorosilyl)bis(triphenylphosphine)platinum(II) (2), ir(KBr): 1240 cm^{-1} (δ(Si-CH_3)), 800 cm^{-1} (δ(Si-CH_3), doublet), and 450 cm^{-1} (ν(Pt-P)). 2 was sparingly soluble in benzene and gave poor nmr spectrum. It was very unstable in chloroform and dichloromethane solution.

When trichlorosilane was used instead of methyldichlorosilane, *cis*-bis(trichlorosilyl)bis(triphenylphosphine)platinum(II) (3) was the only product, whether 1-hexene was present or not. 2[14b] and 3[16] have been obtained by treatment of PtL_4 with the corresponding hydrosilanes. It seems most likely that trichlorosilane is so reactive towards the hydridosilylplatinum(II) as well as $PtL_2(C_2H_4)$ that it readily enters further into oxidative addition followed by elimination of hydrogen from the resulting Pt(IV)

species to give the observed 3 (Scheme I).

Scheme I

$$L_2Pt(C_2H_4) \xrightarrow[-C_2H_4]{HSiCl_2R} L_2PtH(SiCl_2R) \xrightarrow[-H_2]{HSiCl_2R} L_2Pt(SiCl_2R)_2$$

1, R = Me

2, R = Me

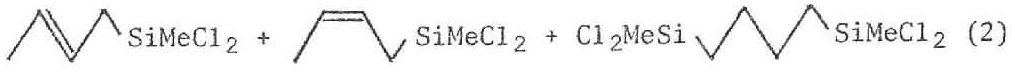
3, R = Cl

In cases where trimethylsilane or dimethylchlorosilane was used under the conditions for hydrosilylation of 1-hexene, $PtL_2(C_2H_4)$ was immediately converted into red-brown crystals which were very soluble in benzene. This complex did not contain silyl groups, analyzed as $[PtL(C_6H_6)]_x$ (4). Although 4 could not be fully characterized, a cluster structure may be suggested. Gillard *et al.*[17] have briefly described the preparation of "$(PtL)_4$"and "$(PtL_2)_3$", which were identified to be $[PtPPh_2$-$(C_6H_4$-$PPh_2)]_x$ by reinvestigation.[18] Tsuji and his coworkers[6b] have found that the reaction of tetrakis(triphenylphosphine)-palladium(0) with trichlorosilane at room temperature gives hydridotrichlorosilylbis(triphenylphosphine)palladium(II), which readily decomposes on heating to yield yellow crystals, a cluster compound of bis(triphenylphosphine)palladium.

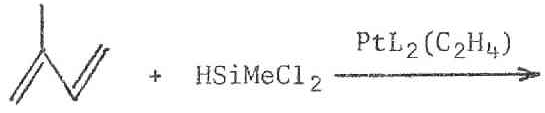
In view of these observations, it may reasonably be concluded that the order of stabilities of the silylplatinum complexes ($SiCl_3$ > $SiMeCl_2$ > $SiMe_2Cl$ ~ $SiMe_3$) formed by treatment of $PtL_2(C_2H_4)$ with hydrosilanes is the same as that observed for silylrhodium complexes prepared starting with $RhClL_3$.[9]

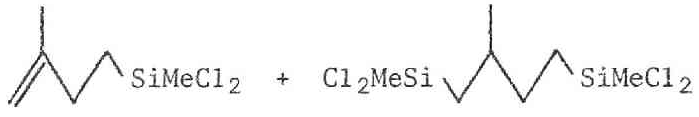
Hydrosilylation of 1,3-dienes in the presence of $PtL_2(C_2H_4)$ was also examined. The reaction of butadiene with methyldichlorosilane at 80° gave not only *trans*- and *cis*-1-methyldichlorosilyl-2-butene (5) (in a ratio of 85:15) but 1,4-bis(methyldichloro-

silyl)butane (6) in a ratio of 4:3 (eq. 2). It should be mentioned that nickel[7] and palladium[6,19] complex-catalyzed hydrosilylations of butadiene with methyldichlorosilane or trichlorosilane give exclusively 5 or its trichlorosilyl analog and that the isomeric composition of 5 is very favorable to the *cis* isomer. In the reaction with isoprene, 2-methyl-4-methyldichlorosilyl-1-butene (7) and 2-methyl-1,4-bis(methyldichlorosilyl)butane (8) (7:1) were obtained (eq. 3).



trans-5 *cis*-5 6 (2)





7 8 (3)

It is noteworthy that in the case of isoprene the only monoadduct formed was the 1,2-addition product 7[20] which arises from addition to a less substituted double bond, and that even when an excess of the diene was used the di-adduct 8 was always formed in considerable amounts. 7 has never been formed from the nickel or palladium catalyzed reaction.

Since $PtL_2(C_2H_4)$ cannot catalyze the addition of hydrosilanes to internal olefins at least at 80°, and isomerization

of 1-hexene to 2-isomers does occur even slowly under the conditions used, some features may be drawn from the results obtained here: the fact that no 1,4-adduct of isoprene was obtained may be ascribed to a less favorable reaction of isoprene as a 1,3-diene with the platinum catalyst than as a terminal olefin. It follows in the case of butadiene also that 5 (*trans/cis* = 85/15) may result from, at least partly, an isomerization of 4-methyldichlorosilyl-1-butene formed initially, at the same time the latter being ready to undergo further addition of methyldichlorosilane to give the di-adduct 6.

In this context, it is feasible to conclude that 7 as a major product in the present hydrosilylation of isoprene is hardly isomerized for steric reasons. Nickel[7,21] and palladium[6,19] complexes catalyze definitely a 1,4-addition of hydrosilanes to isoprene, which fact suggests the intervention of π-allylic metal intermediates. Such π-allylic platinum complexes are known to be rather unusual.

EXPERIMENTAL

Hydrosilylation of olefins catalyzed by platinum(0) complexes

1. Simple olefins. An olefin (3.5 mmol), a hydrosilane (4.0 mmol), and the catalyst (2×10^{-3} mmol) dissolved in benzene (1.0 ml) were sealed together in an evacuated glass tube and heated at 90° or at 140° for a given time. Products were isolated by distillation, and characterized by nmr spectral studies and elemental analyses for new compounds. Reaction conditions, products, and yields are summarized in Table I.

Analytical and ^1H nmr spectral data for new compounds are shown below.

n-$C_6H_{13}SiMe_2Et$. *Anal* Calcd for $C_{10}H_{24}Si$: C, 69.67; H, 14.03.... Found: C, 69.88; H, 14.23. Nmr(CCl_4/C_6H_6): δ -0.03 (s, $SiCH_3$),

0.4-1.7 (m, others).

n-$C_6H_{13}SiMe_2Cl$. *Anal* Calcd for $C_8H_{19}ClSi$: C, 53.75; H, 10.71. Found: C, 54.82; H, 11.17. Nmr(CCl_4/TMS): δ 0.37 (s, $SiCH_3$), 0.5-1.7 (m, others).

n-$C_6H_{13}SiMe(OEt)_2$. *Anal* Calcd for $C_{11}H_{26}O_2Si$: C, 60.49; H, 12.00. Found: C, 60.93; H, 12.29. Nmr(CCl_4/TMS): δ 0.03 (s, $SiCH_3$), 1.18 (t, J = 6.8 Hz, OCH_2CH_3), 3.69 (q, OCH_2), 0.4-0.6 (m, others).

$EtMe_2SiCH_2CH_2SiMeCl_2$. *Anal* Calcd for $C_7H_{18}Cl_2Si_2$: C, 36.67; H, 7.91. Found: C, 36.96; H, 8.16. Nmr(CCl_4/C_6H_6): δ 0.02 (s, $Si(CH_3)_2Et$), 0.79 (s, $Si(CH_3)Cl_2$), 0.5-1.4 (m, others).

2. Butadiene. In a degassed glass tube, a mixture of 1.9 g (3.5 mmol) of butadiene and 4.0 g (3.5 mmol) of methyldichlorosilane was heated at 80° for 20 hr in the presence of 1.5 mg (2×10^{-3} mmol) of bis(triphenylphosphine)ethyleneplatinum. The products were isolated by fractional distillation to give 2.2 g (38%) of 1-methyldichlorosilyl-2-butene (5) and 2.9 g (29%) of 1,4-bis(methyldichlorosilyl)butane (6); 5, bp 70-75° (15 mm), (lit.[22] bp 143° (758 mm)). Glc analysis indicated that 5 consists of *trans*- and *cis*-isomers in a ratio of 85:15. Nmr(CCl_4/TMS): *trans*-5; δ 0.76 (s, 3H, $SiCH_3$), 1.70 (m, 3H, CCH_3), 2.00 (m, 2H, CH_2Si), and 5.45 (m, 2H, CH=). *cis*-5; δ 0.77 (s, 3H, $SiCH_3$), 1.66 (m, 3H, CCH_3), 2.09 (m, 2H, CH_2Si), and 5.60 (m, 2H, CH=). *Anal* Calcd for $C_5H_{10}Cl_2Si$: C, 35.51; H, 5.96. Found: C, 35.35; H, 6.01. 6, bp 130-133° (2 mm), nmr(CCl_4/TMS): δ 0.80 (s, 6H, $SiCH_3$) and 1.1-1.9 (m, 8H, CH_2). *Anal* Calcd for $C_6H_{14}Cl_4Si_2$: C, 25.36; H, 4.97. Found: C, 26.62; H, 5.05.

3. Isoprene. Similarly starting with isoprene (2.4 g; 3.5 mmol) and methyldichlorosilane (4.0 g; 3.5 mmol), there were obtained, after fractional distillation, 4.5 g (70%) of 2-methyl-4-methyldichlorosilyl-1-butene (7) and 0.9 g (9%) of 2-methyl-1,4-bis(methyldichlorosilyl)butane (8). 7, bp 83° (15 mm), (lit.[14a] bp 155° (727 mm)), nmr(CCl_4/TMS): δ 0.78 (s, $SiCH_3$),

1.75 (s, CCH_3), and 4.70 (broad s, $=CH_2$), and other protons as diffused multiplets. 8, bp 130-135° (2 mm), (lit.[14a] bp 75° (0.01 mm)), nmr(CCl_4/TMS): 0.79 and 0.82 (a pair of s, $SiCH_3$) and 1.07 (d, J = 6.5 Hz, $CHCH_3$), and other protons as diffused multiplets.

Preparation of silylplatinum(II) complexes

1. Hydridomethyldichlorosilylbis(triphenylphosphine)platinum(II) (1). In a glass tube were placed 0.29 g (3.5 mmol) of 1-hexene, 0.46 g (4.0 mmol) of methyldichlorosilane, and 100 mg (0.13 mmol) of bis(triphenylphosphine)ethyleneplatinum dissolved in 0.5 ml of dry benzene. The mixture was degassed by several freeze-thawings *in vacuo*. The tube was sealed with evacuation and heated at 90° for 18 hr. White crystals began to precipitate from the reaction mixture in 30 min. After removal of benzene and excess methyldichlorosilane, the crystals were filtered off under nitrogen, washed with a small amount of benzene, and dried *in vacuo* to give 67 mg (70%) of 1, mp 210-215° (in a sealed tube), (lit.[14b] mp 186°). *Anal* Calcd for $C_{37}H_{34}Cl_2P_2SiPt$: C, 53.24; H, 4.11; P, 7.42. Found: C, 53.21; H, 4.27; P, 6.80. Ir data are shown in the text. ^1H nmr spectrum could not be obtained since 1 was sparingly soluble in benzene and chloroform.

2. Bis(methyldichlorosilyl)bis(triphenylphosphine)platinum(II) (2). In a similar manner as above, a mixture of 8.0 g (7.0 mmol) of methyldichlorosilane and 300 mg (0.40 mmol) of bis(triphenylphosphine)ethyleneplatinum dissolved in 1.5 ml of benzene was heated at 90° for 4 days. Hydrogen was evolved and pale yellow crystals precipitated. The crystals formed were washed with benzene and dried *in vacuo* to give 190 mg (50%) of 2, mp 200-210° (in a sealed tube),(lit.[14b] mp 179°). *Anal* Calcd for $C_{38}H_{36}Cl_4P_2Si_2Pt$: C, 48.16; H, 3.83; P, 6.64. Found: C, 48.03; H, 3.95; P, 5.20. Ir data are shown in the text.

3. Bis(trichlorosilyl)bis(triphenylphosphine)platinum(II)

(3). Similarly, from a mixture of 0.14 g (1.0 mmol) of trichlorosilane, 0.8 g (1.0 mmol) of 1-hexene, and 200 mg (0.27 mmol) of bis(triphenylphosphine)ethyleneplatinum dissolved in 5.0 ml of benzene, 150 mg (55%) of 3 was obtained as white powders, mp 239-242°, (lit.[16] 210-212°), ir(KBr): 553 cm^{-1} (ν(Si-Cl)) and 450 cm^{-1} (ν(Pt-P)). *Anal* Calcd for $C_{36}H_{30}Cl_6Si_2P_2Pt$: C, 43.74; H, 3.06. Found: C, 43.25; H, 3.34.

4. Cluster platinum complex (4). In a degassed glass tube, a mixture of 0.30 g (4.0 mmol) of trimethylsilane, 0.29 g (3.5 mmol) of 1-hexene, and 200 mg (0.27 mmol) of bis(triphenylphosphine)ethyleneplatinum dissolved in 1.0 ml of benzene was heated at 90° for 20 hr. The solution immediately turned dark red. The resulting solution was condensed *in vacuo* to a minimum volume. Brown-red crystals formed were collected, washed with a small amount of hexane, and dried *in vacuo* to give 120 mg of 4, mp > 280° (in a sealed tube). ^1H nmr and ir spectra showed the absence of trimethylsilyl groups. 4 has empirical formula of $[Pt(PPh_3)C_6H_6]_x$ on the basis of elemental analysis. *Anal* Calcd for $C_{24}H_{21}PPt$: C, 53.83; H, 3.95; P, 5.78. Found: C, 54.48; H, 3.99; P, 6.92.

REFERENCES AND NOTES

1. A preliminary communication has appeared in J. Organometal. Chem., 28, C37 (1971).
2. For a review: C. Eaborn and R. W. Bott, in A. G. McDiarmid Ed., "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, Marcel Dekker, New York, N. Y., 1968, pp. 213-278.
3. J. W. Ryan and J. L. Speier, J. Org. Chem., 31, 2698 (1966), and their previous papers cited therein.
4. A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 87, 16

(1965).

5. a) S. Takahashi, T. Shibano, and N. Hagihara, Chem. Commun., 161 (1969); b) S. Takahashi, T. Shibano, H. Kojima, and N. Hagihara, Organometal. Chem. Syn., 1, 193 (1970/1971).
6. a) J. Tsuji, M. Hara, and K. Ohno, Tetrahedron, 30, 2143 (1974); b) M. Hara, K. Ohno, and J. Tsuji, Symposium on Organometallic Compounds, Kiryu, Japan, 1970; Abstr., p.164.
7. Y. Kiso, K. Tamao, and M. Kumada, J. Organometal. Chem., 76, 95 (1974), and their previous papers cited therein.
8. E. W. Bennett and P. J. Orenski, J. Organometal. Chem., 28, 137 (1971).
9. a) F. de Charentenay, J. A. Osborn, and G. Wilkinson, J. Chem. Soc. A, 787 (1968); b) R. N. Haszeldine, R. V. Parish, and D. J. Parry, J. Organometal. Chem., 9, 31 (1967); *idem*, J. Chem. Soc. A, 683 (1969).
10. a) A. J. Chalk, J. Organometal. Chem., 21, 207 (1970); b) A. J. Chalk, Trans. N. Y. Acad. Sci., Ser. II., 32, 481 (1970).
11. Although Chalk and Harrod[4] studied the interaction of the phosphine-platinum complex with various hydrosilanes, they did not mention its catalytic activity.
12. K. Yamamoto, H. Okinoshima, and M. Kumada, to be published.
13. C. D. Cook and G. S. Jauhal, J. Amer. Chem. Soc., 90, 1464 (1968).
14. a) W. Fink, Helv. Chim. Acta, 54, 1304 (1971); b) W. Fink and A. Wenger, *ibid.*, 54, 2186 (1971).
15. C. Eaborn, A. Pidcock, and B. Ratcliff, J. Organometal. Chem., 43, C5 (1972).
16. J. Chatt, C. Eaborn, and P. N. Kapoor, J. Organometal. Chem., 13, 21 (1968); *idem*, J. Chem Soc. A, 881 (1970).
17. P. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, Chem. Commun., 869 (1966).

18. F. Glockling, T. McBride, and R. J. I. Pollock, J. C. S. Chem. Commun., 650 (1973).

19. V. Vaisarava, M. Capka, and J. Hetflejs, Synth. Inorg. Metal-org. Chem., 2, 289 (1972).

20. Post *et al.* [J. Org. Chem., 26, 4000 (1961)] have claimed that chloroplatinic acid-catalyzed addition of methyldichlorosilane to isoprene takes place in a 1,4-fashion to give 1-methyldichlorosilyl-2-methyl-2-butene (9) in 60% yield, along with a polymeric residue formed upwards of 20% by weight. We are inclined to insist that the product is not really 9 but a 1-silyl-3-methyl-2-butene by an isomerization of 7 under forced conditions (165°, 17 hr), and that significant amounts of the residue not characterized would be the di-adduct 8.

21. M. F. Lappert, T. A. Nile, and S. Takahashi, J. Organometal. Chem., 72, 425 (1974).

22. A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and G. O. Odabashyan, Izv. Akad. Nauk, S.S.S.R., 1206 (1957) [Chem. Abstr., 52, 6160 (1958)].

Chapter 2

Catalytic Asymmetric Hydrosilylation of Olefins. I. Chiral Phosphine-Platinum(II) Complexes as Hydrosilylation Catalysts[1]

SUMMARY

Several platinum(II) complexes containing chiral phosphines, (*R*)-benzylmethylphenylphosphine (BMPP), (*R*)-methylphenyl-*n*-propylphosphine (MPPP), and menthyldiphenylphosphine (MDPP), were prepared. Catalytic asymmetric hydrosilylation has been achieved for the first time in the reaction of methyldichlorosilane with 1,1-disubstituted prochiral olefins, α-methylstyrene, 2,3-dimethyl-1-butene, and 2-methyl-1-butene, using a platinum catalyst precursor, $[L^*PtCl_2]_2$ (L* = BMPP and MPPP), the resulting adduct of the type $RMe\overset{*}{C}HCH_2SiMeCl_2$ (R = Ph, *i*-Pr, and Et) being obtained, respectively. When trichlorosilane was used, the asymmetric addition reaction was always accompanied by isomerization or dimerization of the olefins. The chiral platinum complex-catalyzed addition-cyclization of 4-pentenyldimethylsilane also gave rise to an optically active 2-methyl-1-silacyclopentane derivative despite a simple terminal olefin of the substrate.

INTRODUCTION

There has been a considerable interest in hydrosilylation of olefins in the presence of various Group VIII metal complexes as homogeneous catalysts.[2] A mechanism for the platinum(II) complex-catalyzed hydrosilylation has been proposed on the basis

of coordination catalysis of d^8 metal complexes.[3,4] It is similar to the mechanism proposed for rhodium(I)-catalyzed hydrogenation reactions mostly advanced by Wilkinson and his coworkers.[5] In the last few years, several asymmetric hydrogenation catalysts, all of which are chiral phosphine complexes of rhodium, have been described.[6]

In view of the formal resembrance in mechanisms between transition metal-catalyzed hydrogenation and hydrosilylation, it seemed of particular interest to explore asymmetrically catalyzed hydrosilylation of prochiral olefins using d^8 metal complexes with chiral ligands.

Few of the platinum complexes with phosphine ligands as effective catalysts for hydrosilylation had been recorded in the literature until 1971, when Fink[7a] and we[7b] found independently that some of them can catalyze the reaction, whereas there appeared several papers in 1968-1970 which dealt with certain phosphine complexes of palladium,[8] nickel,[9] and rhodium[10] as the catalysts.

The present study was undertaken to investigate the use of chiral phosphine-platinum(II) complexes as asymmetric hydrosilylation catalysts with particular emphasis on the addition of methyldichlorosilane to 1,1-disubstituted olefins. Some nickel and rhodium complexes with chiral phosphines as catalysts will be described in the succeeding chapters.

RESULTS AND DISCUSSION

Platinum(II) complexes with chiral phosphines as catalysts

cis-Dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II)[11] is known to undergo exchange of the coordinated ethylene with a prochiral olefin (such as *tert*-butylethylene and *trans*-2-butene), while giving rise to an asymmetric induction of the latter.

Although this complex showed an efficient catalytic activity in hydrosilylation of α-methylstyrene and some other olefins (in essentially quantitative yield; see Experimental), the adducts were always racemic.

On the other hand, *cis*-dichloro(ethylene)phosphineplatinum(II) and related complexes containing a chiral phosphine with an asymmetric phosphorus atom have been found to act as effective catalysts for the aimed reaction, so our interest centered on these complexes.

The optically active platinum(II) complexes were prepared by the following reaction sequences (Chart I).

Chart I

$$2L^* + K_2PtCl_4 \xrightarrow[\text{aq EtOH}]{} \textit{cis}\text{-}L^*{}_2PtCl_2$$

1a, L* = (*R*)-(+)-($PhCH_2$)MePhP (BMPP)
1b, L* = (*R*)-(-)-MePh-*n*-PrP (MPPP)
1c, L* = MenthylPh_2P (MDPP)

$$\textit{cis}\text{-}L^*{}_2PtCl_2 \xrightarrow[Cl_2CHCHCl_2]{PtCl_2,\ 140^\circ} [L^*PtCl_2]_2$$

2a, L* = BMPP
2b, L* = MPPP
2c, L* = MDPP

3a, L* = BMPP
3b, L* = MPPP
3c, L* = MDPP

$$3a + 2C_2H_4 \xrightarrow[C_6H_6]{} 2\textit{cis}\text{-}(C_2H_4)L^*PtCl_2$$

4a, L* = BMPP

Dichlorobis[(*R*)-benzylmethylphenylphosphine (BMPP)]di-μ-chlorodiplatinum(II) (3a) and its (*R*)-methylphenyl-*n*-propylphosphine (MPPP) analog (3b) were prepared according to a modified procedure of Orchin *et al.*[12] involving reaction of the mononuclear complex, 2a or 2b, and platinum chloride in tetrachloroethane solution, instead of melting them together as originally reported by Chatt and Venanzi.[13] This was in order to avoid possible racemization of the phosphine ligand, since the optically active phosphine 1b is found[14] to undergo considerable racemization with a half-life of 5 hr at 130°. It was confirmed that no appreciable decrease in optical activity of 2a dissolved in tetrachloroethane was heated even at 155° for 15 hr.

The chlorine-bridged complex of menthyldiphenylphosphine (MDPP) (3c) was also prepared in order to compare the effectiveness of asymmetric induction in the hydrosilylation, since a complex with ligands that are asymmetric remote from phosphorus does fulfil the necessary conditions for asymmetric catalysis.[6]

One particular ethylene complex of the *cis* configuration 4a was prepared by direct interaction of ethylene with 3a under mild conditions.[15]

Of these platinum complexes prepared here, 2a-2c were found to be ineffective as catalyst precursors (probably due to insolubility). Complex 4a exhibited an efficient catalytic activity for hydrosilylation of various prochiral olefins. 3a was as effective a chiral catalyst precursor as the ethylene complex 4a, as would be expected from its possible interaction with a substrate olefin to form the same catalyst species.

Physical data of all complexes thus prepared are listed in Table I.

Asymmetric hydrosilylation of 1,1-disubstituted olefins

In typical runs, a mixture of an olefin and an equivalent of methyldichlorosilane was heated in the presence of a catalyst

Table I. Melting Points and Optical Rotations of Platinum(II) Complexes of Chiral Phosphines.

No.	Complex Abbreviation	Color	Mp (°C)[a]	$[\alpha]_D^{15}$ [b] deg.
2a	*cis*-$(R_3^*P)_2PtCl_2$[c]	colorless	249-250	-57.4[d]
2b	*cis*-$(R_3'^*P)_2PtCl_2$[e]	colorless	171-172	-24.6
2c	*cis*-$(MenPh_2P)_2PtCl_2$[f]	pale yellow	243-244	-145
3a	$[R_3^*PPtCl_2]_2$[c]	yellow	125-127	—
3b	$[R_3'^*PPtCl_2]_2$[e]	orange yellow	134-135	-15.0
3c	$[MenPh_2PPtCl_2]_2$[f]	off-white	299-300	-27.0[g]
4a	*cis*-$(C_2H_4)R_3^*PPtCl_2$[c]	pale yellow	—	-49.4[g]

[a] Measured in a sealed tube. [b] In dichloromethane (*c* 1.00-1.60). [c] R_3^*P = (*R*)-(+)-$(PhCH_2)MePhP$ (81% optical purity) (ref. 25). [d] -56.7° when R_3^*P (79% optical purity) was used. [e] $R_3'^*P$ = (*R*)-(-)-MePh-*n*-PrP (93% optical purity) (ref. 25). [f] $MenPh_2P$ = (-)-Menthyldiphenylphosphine. [g] Analytically not purified.

(10^{-3} mole per mole of olefin) at 40° over a period of 24 hr. The hydrosilylation proceeded smoothly (eq. 1).[16] The addition

$$RMeC{=}CH_2 + HSiMeCl_2 \xrightarrow{\text{chiral Pt}} RMe\overset{*}{C}HCH_2SiMeCl_2 \qquad (1)$$

5a, R = Ph — 6a, R = Ph
5b, R = *i*-Pr — 6b, R = *i*-Pr
5c, R = Et — 6c, R = Et

products were isolated by distillation in moderate yields and characterized by ir and nmr spectral data and elemental analyses for new compounds. Optical yields of the products were deter-

mined, after methylation to their trimethylsilyl derivatives, by comparison of specific rotations of the latter with those of the authentic substances, which were prepared by the unambiguous route shown below (eq. 2). Actual conversions were carried out

$$RMe\overset{*}{C}HCH_2Cl \xrightarrow[2.\ ClSiMe_3]{1.\ Mg\text{-}THF} RMe\overset{*}{C}HCH_2SiMe_3 \qquad (2)$$

7a, R = Ph	8a, R = Ph
7b, R = *i*-Pr	8b, R = *i*-Pr
7c, R = Et	8c, R = Et

with chlorides of lower activity and the maximum rotation of the resulting trimethylsilyl derivatives 8a-8c was calculated on the basis of optical purity of the starting chloride.

The data obtained for asymmetric hydrosilylation of 5a-5c and for the authentic substances 8a-8c are summarized in Tables II and III, respectively.

Although the extent of asymmetric induction in the hydrosilylation was considerably low[16] and a nickel complex of the same chiral phosphine as one used here has been found to catalyze the reaction with higher asymmetric bias[17] than the present platinum(II) system, the fact that the platinum complexes used contain one chiral phosphine molecule may allow one to discuss the actual contribution of the chiral information of the catalyst to the present asymmetric hydrosilylation. First, a system with one asymmetric center as close to the platinum atom as possible may be advantageous for the purpose of sustaining the asymmetric bias, though this is not always necessary for asymmetric synthesis in general.[18] Morrison and coworkers[19] have reported that a chiral rhodium complex with the neomenthyldiphenylphosphine (NMDPP) ligand, which is not asymmetric at phosphorus, is very effective as an asymmetric homogeneous hydrogenation catalyst.

Table II. Asymmetric Hydrosilylation of Olefins with $HSiMeCl_2$ Catalyzed by Chiral Phosphine-Platinum(II) Complexes at 40°.

Olefin	Catalyst[a]	Yield (%)	$[\alpha]_D^{15}$, deg of product[b]	$[\alpha]_D^{15}$, deg methylated[b]	Optical yield (%)[c] (Configuration)
$PhMeC=CH_2$	3a	56	+1.65	+1.03	5.2 (*R*)
$PhMeC=CH_2$	4a	43	+1.93	+1.20	6.1 (*R*)
$PhMeC=CH_2$	3b	64	+0.38		1.1 (*R*)
$PhMeC=CH_2$	3c	33[d]	0		—
i-$PrMeC=CH_2$	3a	83	-0.17	-0.27	1.4 (*R*)
i-$PrMeC=CH_2$	4a	76	-0.16	-0.24	1.2 (*R*)
i-$PrMeC=CH_2$	3b	86	-0.19		1.3 (*R*)
i-$PrMeC=CH_2$	3c	70[e]	-0.14		0.9 (*R*)
$EtMeC=CH_2$	3a	68	-0.13	-0.15	1.2 (*R*)
$EtMeC=CH_2$	4a	69	-0.12	-0.14	1.1 (*R*)
$EtMeC=CH_2$	3b	55	-0.08		0.6 (*R*)
$EtMeC=CH_2$	3c	35[e]	0		—

[a] See Table I. [b] Neat. [c] Based on the maximum rotation of authentic samples and calibrated for the optical purity of the chiral phosphines used. [d] Heated at 120° for 60 hr. [e] Heated at 90° for 40 hr.

Table III. Data of Maximum Rotation of the Authentic Samples.

Compound	Bp (°C/mm)	d_4^{15}	n_D^{15}	$[\alpha]_D^{15}$, max[a]
(*R*)-$PhMeCHCH_2SiMe_3$	98/17	0.8681	1.4900	+24.3
(*R*)-*i*-$PrMeCHCH_2SiMe_3$	149.5	0.7557	1.4232	-24.1
(*S*)-$EtMeCHCH_2SiMeCl_2$[b]	77/37	1.0166	1.4408	+13.1
(*S*)-$EtMeCHCH_2SiMe_3$	132.0	0.7420	1.4158	+16.0

[a] Neat and based on the optical purity of starting chlorides used. [b] Cl_3SiMe was used instead of $ClSiMe_3$.

However, a platinum(II) complex with epimeric chiral phosphine 1c proved to be less useful for the asymmetric hydrosilylation studied here. Second, in Table II it is seen that the extent of asymmetric induction depends on the structure of both the phosphine ligand with an asymmetric phosphorus atom and the olefinic substrate: 1a is positively a better chiral ligand than 1b to induce asymmetry in hydrosilylation of α-methylstyrene (5a), In addition, a preferred configuration of these addition products, 6a-6c, was consistently of the *R* isomer. Thus, in the light of current views of the mechanisms of metal-catalyzed hydrosilylation,[3,4] we may assume that, in all cases, a similar stereochemical sequence of coordination of the olefin to platinum followed by addition of the silane occurs, *viz.* a similar diastereomeric transition state is involved. Finally, as far as chiral phosphines are concerned, the catalytic asymmetric hydrogenation is, at present, restricted to the use of rhodium complexes as catalysts. In this context, it is of interest to note that, in contrast to the hydrogenation, the hydrosilylation using various chiral phosphine complexes of nickel,[17] palladium,[18] as well as rhodium[20] as catalyst precursors can always exhibit some extent of asymmetric induction, which will be described in

the succeeding chapters.

Effects of silanes used on the asymmetric hydrosilylation

Methyldichlorosilane was by far the most reactive in the hydrosilylation of 1,1-disubstituted olefins (5a-5c). Trialkylsilanes did not add at all to such olefins with the chiral platinum catalysts even at 120°, whereas the addition of trimethylsilane and diethylmethylsilane to 1-hexene (but not to internal olefins such as 2-hexene) proceeded smoothly at 40° in the presence of *trans*-dichloro(ethylene)pyridineplatinum(II)[21] or bis(triphenylphosphine)ethyleneplatinum(0)[7] as catalyst. Moreover, in a case where trichlorosilane was used, hydrosilylation of 5a-5c gave rather complicated results, involving some isomerization or dimerization of olefins. Thus, in the addition of trichlorosilane to 5a in the presence of 3a or 4a at 90°, a 1:2 adduct (9) was a major product, which was isolated optically inactive in 52% yield (eq. 3).

$$\underset{\text{5a}}{\text{PhMeC=CH}_2} + \text{HSiCl}_3 \xrightarrow{\text{3a}} \underset{\text{9}}{\text{PhCH}(\text{CH}_2\text{SiCl}_3)\text{CH}_2\text{CMe}_2\text{Ph}} \qquad (3)$$

When 5c was used, two products were obtained in comparable amounts (54% combined yield), one being the expected 2-methylbutyltrichlorosilane (10) and the other, isoamyltrichlorosilane (11). The latter obviously came from 3-methyl-1-butene, which was formed by isomerization of 5c under the conditions used, and

$$\underset{\text{5c}}{\text{EtMeC=CH}_2} + \text{HSiCl}_3 \xrightarrow{\text{4a}} \underset{\text{10}}{\text{EtMeCHCH}_2\text{SiCl}_3} + \underset{\text{11}}{\text{Me}_2\text{CHCH}_2\text{CH}_2\text{SiCl}_3} \qquad (4)$$

might be sterically less hindered with respect to the addition reaction of the silane (eq. 4). Finally, with 5b the hydrosilylation afforded a sole product, slightly active 2,3-dimethylbutyltrichlorosilane, in 70% yield. Although some isomerization would also take place in this case, the isomerized olefin is identical with the original one. After methylation of the adduct, the optical yield was found to be 0.8% of the *R* isomer.

All results described here indicate a significant electronic rather than steric effect of the substituents of silanes on the platinum-catalyzed hydrosilylation. In Chapter 1,[7b] it has been claimed that the stability of the silylplatinum intermediates formed upon treatment of $Pt(PPh_3)_2(C_2H_4)$ with a series of silanes is in the order $SiCl_3 > SiMeCl_2 > SiMe_3$, which is the same as that for the oxidative addition of these silanes to $RhCl(PPh_3)_3$.[10] This appears to be the reason why some isomerization or dimerization of a substrate olefin on the platinum catalyst precedes the addition of trichlorosilane to the olefin, whereas with methyldichlorosilane there is no appreciable isomerization under the conditions used.

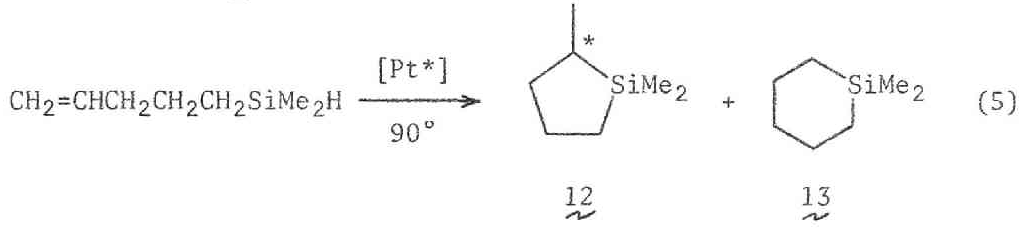
Asymmetric hydrosilylation of other olefins

The asymmetric hydrosilylation of prochiral olefins other than 1,1-disubstituted ones was unsuccessful, since highly substituted olefins did not undergo addition of methyldichlorosilane under the conditions used.

With a simple terminal olefin a terminal adduct is usually the major product. Hydrosilylation of styrene with methyldichlorosilane readily took place in the presence of 3a even at room temperature to give 2-phenylethylmethyldichlorosilane (50% yield) and 1-phenylethylmethyldichlorosilane (20% yield),[22] but the latter was optically inactive.

We have observed the asymmetric induction in one particular

case, where a ring-closure occurs to give a 2-methyl-1-silacyclopentane. Thus, the hydrosilylation of 4-pentenyldimethylsilane in benzene solution using 3a as catalyst gave two products, 1,1,2-trimethyl-1-silacyclopentane (12),[23] $[\alpha]_D^{20}$ +0.24° (neat), and 1,1-dimethyl-1-silacyclohexane (13),[23] with the former in an overwhelming quantity. The same two compounds were produced by use of *cis*-dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II) as catalyst, but this chiral amine complex did not cause any asymmetric bias in 12.



(5)

12 13

The preferred formation of the silacyclopentane structure may reasonably be explained by the key intermediate of a six-membered ring involving the platinum center, whereas a seven-membered ring would be required for the formation of the silacyclohexane.[24]

EXPERIMENTAL

General comments

All melting and boiling points are uncorrected. A Varian Aerograph Model 90P, equipped with a 20 ft column packed with Silicone DC-550 (30% on Celite), was used, if necessary, for isolation and purification. Nmr spectra were recorded with a Varian T-60 spectrometer, infrared spectra with a Hitachi EPI G-3 Grating spectrophotometer, and optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter (accuracy ±0.003°).

Preparation of platinum(II) complexes with chiral ligands

1. (-)-*cis*-Dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II). According to a procedure by Panunzi and Paiaro,[11] the purified complex was obtained in 34% overall yield from a reaction of 2.00 g (4.81 mmol) of K_2PtCl_4 with 1.17 g (9.65 mmol) of (*S*)-1-phenylethylamine, $[\alpha]_D^{25}$ -40.2° (neat), followed by incorporation of ethylene; $[\alpha]_D^{25}$ -52.0° (*c* 0.50, acetone) [lit.[11] $[\alpha]_D^{25}$ -53.4° (*c* 1.02, acetone)].

2. Dichlorobis[(*R*)-benzylmethylphenylphosphine]di-μ-chlorodiplatinum(II) (3a). The *cis*-dichlorobis(phosphine)platinum(II) (2a) was prepared from 0.98 g (2.4 mmol) of K_2PtCl_4 and 0.99 g (4.8 mmol) of BMPP[25] ($[\alpha]_D^{20}$ +92.8° (*c* 0.50, toluene) with a 81% optical purity[26] in 30 ml of aqueous ethanol under an argon atmosphere. The precipitate formed was washed with four portions of each 20 ml of ether and dried *in vacuo* to give 1.10 g (66%) of the crude 2a. A pure sample was obtained as colorless needles by recrystallization from CH_2Cl_2/EtOH (1/1): mp 249-250° (in a sealed tube), $[\alpha]_D^{15}$ -57.4° (*c* 1.00, CH_2Cl_2). *Anal* Calcd for $C_{28}H_{30}Cl_2P_2Pt$: C, 48.42; H, 4.35; Cl, 10.21. Found: C, 48.71; H, 4.62; Cl, 10.50.

Repeated recrystallization of this complex should be avoided, since a slight decrease in optical rotation was observed, *e.g.* after the third recrystallization from dry ethanol, $[\alpha]_D^{25}$ -52.0° (*c* 0.30, CH_2Cl_2). This is presumably due to some resolution from possible diastereomers of 2a arising from the partially active phosphine used (81% optical purity).

When 50 mg of 2a dissolved in 10 ml of tetrachloroethane, $[\alpha]_D^{25}$ -52.4° (*c* 0.50), was heated in a degassed sealed glass tube at 155° (boiling anisole bath) for 15 hr, the resulting slightly colored solution showed an optical rotation of -54.0°.

According to a procedure by Orchin *et al.*,[12] 0.58 g (0.84 mmol) of 2a and 0.28 g (1.05 mmol) of platinum(II) chloride sus-

pended in 24 ml of freshly distilled tetrachloroethane was heated at reflux temperature with occasional shaking for 1.5 hr under argon atmosphere. The resulting solution was separated by filtration from the black residue, and the filtrate was condensed *in vacuo* to a minimum volume. By dissolving the crude product in dichloromethane (3 ml), adding 40 ml of *n*-hexane, 0.66 g (82%) of pure 3a as a yellow powder was obtained, mp 125-127°. *Anal* Calcd for $C_{28}H_{30}Cl_4P_2Pt_2$: C, 35.02; H, 3.14; Cl, 14.77. Found: C, 35.98; H, 3.45; Cl, 13.89.

3. *cis*-Dichloro(ethylene)[(*R*)-benzylmethylphenylphosphine]-platinum(II) (4a). The reported procedure by Chatt *et al.*[15] for preparing ethylene complexes was modified as follows. A solution of 0.29 g (0.30 mmol) of 3a in 10 ml of purified benzene was placed in a micro autoclave with a glass lining, and magnetically stirred with ethylene at 40 kg/cm^2. After three days, 0.25 g (82%) of crude 4a was collected. It was too soluble in usual organic solvents to purify by further recrystallization. *Anal* Calcd for $C_{16}H_{19}Cl_2PPt$: C, 38.37; H, 3.82; Cl, 14.16. Found: C, 40.30; H, 4.33; Cl, 13.05.

4. Dichlorobis[(*R*)-methylphenyl-*n*-propylphosphine]di-μ-chlorodiplatinum(II) (3b). In a similar manner to that described for 2a, *cis*-dichlorobis[(*R*)-methylphenyl-*n*-propylphosphine]platinum(II) (2b) was prepared from 1.00 g (2.4 mmol) of K_2PtCl_4 and 0.80 g (4.8 mmol) of MPPP (93% optical purity[26]) in 70% yield. *Anal* Calcd for $C_{20}H_{30}Cl_2P_2Pt$: C, 40.14; H, 5.05; Cl, 11.85. Found: C, 40.20; H, 5.22; Cl, 12.13.

Complex 2b (0.60 g, 1.00 mmol) was then reacted with 0.33 g (1.23 mmol) of $PtCl_2$ in 25 ml of freshly distilled $Cl_2CHCHCl_2$ to give 0.61 g (70%) of crude 3b. It was dissolved in a hot mixture of CH_2Cl_2 (10 ml) and *n*-hexane (15 ml) and subsequently part of CH_2Cl_2 was removed by distillation until clouding began. Keeping the mixture in a refrigerator gave pure 3b as orange yellow

prisms. *Anal* Calcd for $C_{20}H_{30}Cl_4P_2Pt_2$: C, 27.79; H, 3.50; Cl, 16.41. Found: C, 27.74; H, 3.35; Cl, 16.58. Melting points and optical rotations of 2b and 3b are listed in Table I.

5. Dichlorobis[(-)-menthyldiphenylphosphine]di-μ-chloro-diplatinum(II) (3c). Similarly, from 0.50 g (1.2 mmol) of K_2PtCl_4 and 1.85 g (2.6 mmol) of MDPP ($[\alpha]_D^{20}$ -95.7° (*c* 1.07, CH_2Cl_2)),[18] was obtained 0.45 g (41%) of *cis*-dichlorobis[(-)-menthyldiphenylphosphine]platinum(II) (2c) as yellow crystals. *Anal* Calcd for $C_{44}H_{58}Cl_2P_2Pt$: C, 57.77; H, 6.39; Cl, 7.75. Found: C, 57.68; H, 6.38; Cl, 7.70.

2c (0.31 g, 0.34 mmol) was then allowed to react with 0.11 g (0.41 mmol) of $PtCl_2$ to give 0.31 g of crude 3c, which was recrystallized twice from EtOH/CH_2Cl_2 (2/1) to afford 3c as off-white prisms in 56% yield. *Anal* Calcd for $C_{44}H_{58}Cl_4P_2Pt_2$: C, 44.75; H, 4.69; Cl, 12.01. Found: C, 41.38; H, 4.17; Cl, 13.67.

Asymmetric hydrosilylation of 1,1-disubstituted olefins

1. α-Methylstyrene (5a). (a) With methyldichlorosilane. The following procedure for an asymmetric hydrosilylation of 5a is typical. In a sealed degassed glass tube, a mixture of 3.60 g (30 mmol) of 5a, 3.50 g (30 mmol) of methyldichlorosilane and 10 mg (*ca.* 2×10^{-2} mmol) of 4a was heated at 40° over a period of 24 hr. The product was isolated by distillation through a short Vigreux column to give 3.0 g (43%) of 2-phenylpropyldichloromethylsilane (6a), bp 55° (2 mm), n_D^{15} 1.5151, d_4^{15} 1.1110, (lit.[28] bp 148-149° (42 mm), n_D^{25} 1.5082, d_4^{25} 1.100), $[\alpha]_D^{15}$ +1.93° (neat), nmr(CCl_4/TMS): δ 0.34 (s, 3H, $SiCH_3$), 1.37 (d, J = 7.4 Hz, 3H, CCH_3), 1.52 (d, J = 7.4 Hz, 2H, CH_2), 3.11 (ill resolved sextet, 1H, CH), and 7.19 (s, 5H, C_6H_5).

The adduct thus obtained was treated with a large excess of methylmagnesium bromide in ether solution to give 2.4 g (98%) of 2-phenylpropyltrimethylsilane (8a), bp 98° (17 mm), n_D^{15} 1.4900,

d_4^{15} 0.8681 (lit.[28] bp 217° (750 mm), n_D^{25} 1.4841, d_4^{25} 0.8619), $[\alpha]_D^{15}$ +1.20° (neat), nmr(CCl_4/TMS): δ 0.03 (s, 9H, $SiCH_3$), 1.09 and 1.11 (a pair of d, J = 7.6 Hz, 2H, CH_2), 1.45 (d, J = 6.8 Hz, 3H, CCH_3), 3.00 (sextet, 1H, CH), and 7.24 (s, 5H, C_6H_5).

The results of asymmetric hydrosilylation of 5a using 3a, 3b, and 3c as catalyst are listed in Table II.

(b) With trichlorosilane. A mixture of 3.6 g (30 mmol) of 5a, 4.1 g (30 mmol) of trichlorosilane, and 10 mg of 4a was heated at 90° for 24 hr. The reaction mixture was distilled to give 0.2 g (3%) of the expected 2-phenylpropyltrichlorosilane,[29] nmr(CCl_4/TMS): δ 1.42 (d, J = 6.6 Hz, 3H, CCH_3), 1.78 (d, J = 6.8 Hz, 2H, CH_2), 3.19 (ill-resolved sextet, 1H, CH), and 7.29 (s, 5H, C_6H_5); and 3.0 g (52%) of 2,4-diphenyl-4-methylpentyltrichlorosilane (9) as a major product, bp 125-130° (1.3 mm). The latter was converted by methylation into the trimethylsilyl derivative, bp 121-122° (2 mm), n_D^{20} 1.5280, α_D^{20} nil (neat), nmr(CCl_4/C_6H_{12}): δ -0.40 (s, 9H, $SiCH_3$), 1.05 and 1.21 (a pair of s, 6H, CCH_3), 2.01 (d, J = 6.4 Hz, 2H, CCH_2C), and 6.79-7.34 (diffused m, 10H, C_6H_5). *Anal* Calcd for $C_{21}H_{30}Si$: C, 81.22; H, 9.74. Found: C, 80.96; H, 9.82

2. 2,3-Dimethyl-1-butene (5b). (a) With methyldichlorosilane. From a mixture of 2.5 g (30 mmol) of 5b, 3.5 g (30 mmol) of methyldichlorosilane, and 10 mg (2×10^{-2} mmol) of 4a was obtained 4.5 g (76%) of 2,3-dimethylbutylmethyldichlorosilane (6b), bp 69° (16 mm), n_D^{15} 1.4466, d_4^{15} 1.0111, $[\alpha]_D^{15}$ -0.16° (neat), nmr(CCl_4/TMS): δ 0.79 (s, $SiCH_3$) and diffused multiplets of all other protons. *Anal* Calcd for $C_7H_{16}Cl_2Si$: C, 42.21; H, 8.10. Found: C, 42.49; H, 8.29.

The adduct was methylated to give quantitatively 2,3-dimethylbutyltrimethylsilane (8b), bp 149.5°, n_D^{15} 1.4232, d_4^{15} 0.7557, $[\alpha]_D^{15}$ -0.24° (neat), nmr(CCl_4/C_6H_6): δ 0.00 (s, $SiCH_3$) and diffused multiplets. *Anal* Calcd for $C_9H_{22}Si$: C, 68.26; H, 14.00. Found: C, 68.09; H, 13.78.

Other results using 3a-3c as catalysts are given in Table II.

(b) With trichlorosilane. Similarly but with 4.1 g (30 mmol) of trichlorosilane, 2,3-dimethylbutyltrichlorosilane (4.6 g, 70%), bp 75° (22 mm), α_D^{15} -0.012° (0.1 dm, neat), was obtained.

Calcd for $C_6H_{13}Cl_3Si$: C, 32.82; H, 5.97. Found: C, 33.10; H, 6.15. Upon methylation the optical rotation of the trimethylsilyl derivative was $[\alpha]_D^{15}$ -0.15° (neat).

3. 2-Methyl-1-butene (5c). (a) With methyldichlorosilane. From a mixture of 2.1 g (30 mmol) of 5c, 3.5 g (30 mmol) of methyldichlorosilane, and 10 mg of 4a, was obtained 3.8 g (69%) of 2-methylbutylmethyldichlorosilane (6c), bp 62° (22 mm), n_D^{15} 1.4408, d_4^{15} 1.0166 (lit.[30] bp 167°, n_D^{25} 1.4357, d_4^{25} 1.007), $[\alpha]_D^{15}$ -0.12° (neat), nmr(CCl_4/TMS): δ 0.78 (s, $SiCH_3$). Treatment of 6c with excess methylmagnesium bromide in ether gave 2-methylbutyltrimethylsilane (8c), bp 132.0°, n_D^{15} 1.4158, d_4^{15} 0.7420 (lit.[30] bp 134°, n_D^{25} 1.4095, d_4^{25} 0.7343), $[\alpha]_D^{15}$ -0.14° (neat), nmr(CCl_4/TMS): δ -0.03 (s, $SiCH_3$).

Other results using catalyst precursors 3a-3c are given in Table II.

(b) With trichlorosilane. 2-Methylbutyltrichlorosilane (10) and isoamyltrichlorosilane (11) were obtained in 54% combined yield. The glc area ratio of isomeric products was 2:1. The products were methylated to give (by preparative glc) 8c, n_D^{20} 1.4124 (lit.[31] n_D^{20} 1.4120) and isoamyltrimethylsilane, n_D^{20} 1.4089 (lit.[32] n_D^{20} 1.4064).

Asymmetric hydrosilylation of other olefins

1. Styrene. A mixture of 12.5 g (0.12 mol) of freshly distilled styrene, 13.8 g (0.12 mol) of methyldichlorosilane, and 23 mg (2.4×10^{-2} mmol) of 3a (with phosphine of 79% optical purity) was allowed to stand at room temperature for 12 hr. The reaction mixture was distilled, bp 140-143° (37 mm), to give 20.1 g (76% combined yield) of 1-phenylethyl- and 2-phenylethyl-

methyldichlorosilane.[28] The glc area ratio of the isomers was 1:3.2 (ref. 22). The products were methylated and the resultant 1-phenylethyltrimethylsilane was isolated pure by preparative glc. It was optically inactive.

2. 4-Pentenyldimethylsilane. Methyldichlorosilane was treated with 4-pentenylmagnesium bromide to give 64% yield of 4-pentenylchloromethylsilane, bp 143°, nmr(CCl_4/TMS): δ 0.48 (d, J = 3.0 Hz, 3H, $SiCH_3$), 0.6-2.3 (diffused m, 6H, $(CH_2)_3$), 4.77 (d, J = 3.0 Hz, 1H, SiH), and 5.4-6.1 (m, 3H, vinylic protons), ir(neat): 2160 (ν(Si-H)) and 1685 cm^{-1}(ν(C=C)). *Anal* Calcd for $C_6H_{13}ClSi$: C, 48.45; H, 8.81. Found: C, 50.20; H, 9.15. Methylation of this compound gave known 4-pentenyldimethylsilane, bp 118.5-122.5°. *Anal* Calcd for $C_7H_{16}Si$: C, 65.54; H, 12.57. Found: C, 65.40; H, 12.80. (lit.[23] prepared by other ways, bp 120-121°, n_D^{20} 1.4219, d_4^{20} 0.7436).

A mixture of 2.56 g (20 mmol) of 4-pentenyldimethylsilane and 6 mg (10^{-2} mmol) of 3a dissolved in 5 ml of dry benzene was heated at 90° for 40 hr. At this point the addition-cyclization was complete. The glc area ratio of isomeric products was 28:1. 1,1,2-trimethyl-1-silacyclopentane (12) as a major component was isolated by preparative glc, n_D^{20} 1.4402, d_4^{20} 0.7968 (lit.[23] bp 125°, n_D^{20} 1.4380, d_4^{20} 0.7954), $[\alpha]_D^{20}$ +0.24° (neat), nmr(CCl_4/TMS): δ 0.05 and 0.10 (two s, $Si(CH_3)_2$), and 1.00 (broad s, CCH_3), and diffused multiplets assignable to ring protons. The known 1,1-dimethyl-1-silacyclohexane (13) was also obtained in a trace amount.

The same reaction using *cis*-(C_2H_4)[(*S*)-$PhMeCHNH_2$]$PtCl_2$ as catalyst took place readily to give the isomeric products in a ratio of 24:1, but the isolated 1-silacyclopentane derivative was racemic.

Preparation of chiral authentic substances

1. (*R*)-2-Phenylpropyltrimethylsilane (8a). (*R*)-2-Phenyl-

1-propanol ($[\alpha]_D^{20}$ +16.6° (neat), 95.4% optical purity[33]) was converted by treatment with thionyl chloride and pyridine into (*R*)-2-phenyl-1-chloropropane (7a) ($[\alpha]_D^{20}$ +13.4° (neat)), which was contaminated with *ca.* 7% of 1-phenyl-2-chloropropane.[34] The latter was not readily removed but was not objectionable for the desired Grignard reaction.

To a tetrahydrofuran solution of (*R*)-2-phenylpropylmagnesium chloride, prepared from 4.8 g (31 mmol) of the chloride and 0.9 g (37 mg-atom) of magnesium turnings, was added 6.4 g (59 mmol) of trimethylchlorosilane over a period of 0.5 hr. The mixture was heated at reflux for 7 hr, and then hydrolyzed with dilute hydrochloric acid. After working up in the usual manner, fractional distillation gave 1.1 g (20%) of pure (*R*)-2-phenylpropyltrimethylsilane, bp 98° (17 mm), $[\alpha]_D^{15}$ +23.3° (neat). Assuming that an optical purity of the product is exactly the same as that of the starting (*R*)-alcohol, the maximum rotation of 8a is $[\alpha]_D^{15}$ +24.3° (neat).

2. (*R*)-2,3-Dimethylbutyltrimethylsilane (8b). According to a procedure by Pino *et al.*,[35] partially resolved (*R*)-2,3-dimethyl-1-butanol ($[\alpha]_D^{20}$ -2.39° (neat), 43.0% optical purity) was converted into (*R*)-2,3-dimethyl-1-chlorobutane (7b) in 62% yield; bp 120-124°, d_4^{20} 0.8890, $[\alpha]_D^{20}$ -4.22° (neat) (the maximum rotation,[35] $[\alpha]_D^{25}$ -9.91°).

In a similar manner to the preparation of 8a, a reaction of (*R*)-2,3-dimethylbutylmagnesium chloride, prepared from 5.3 g (44 mmol) of 7b (42.6% optical purity), with 17.0 g (65 mmol) of trimethylchlorosilane gave 3.1 g (44%) of crude 8b which was purified by preparative glc, bp 149.5°, $[\alpha]_D^{15}$ -10.3° (neat).

3. (*S*)-2-Methylbutylmethyldichlorosilane (6c) and -trimethylsilane (8c). According to a procedure by Mosher *et al.*,[36] (*S*)-2-methyl-1-butanol of 98% optical purity was converted into (*S*)-2-methylbutyl chloride (7c) in 75% yield, bp 99.0°, $[\alpha]_D^{15}$ +1.68° (neat).

To a solution of 22.5 g (0.15 mol) of freshly distilled trichloromethylsilane dissolved in 130 ml of dry ether-benzene (2:3) was added under gentle refluxing (*S*)-2-methylbutylmagnesium chloride prepared from 16.0 g (0.15 mol) of the chloride in ether. The ether was distilled off through a 30-cm Vigreux column and the residual mass was filtered. The filtrate was distilled under reduced pressure to give 15.5 g (56%) of crude 6c, bp 76.5-77.0° (37 mm), n_D^{15} 1.4408, d_4^{15} 1.0166, $[\alpha]_D^{15}$ +12.8° (neat).

The product (9.2 g) was converted into 8c in 83% yield, bp 132°, n_D^{15} 1.4158, d_4^{15} 0.7420, $[\alpha]_D^{15}$ +15.8° (neat).

The calculated maximum rotations of these authentic substances are given in Table III.

REFERENCES

1. A preliminary communication has appeared in J. Amer. Chem. Soc., 93, 5301 (1971).
2. For relevant reviews: (a) C. Eaborn and B. W. Bott in A. G. MacDiarmid, Ed., "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, Marcel Dekker, New York, N. Y., 1968, pp. 231-263; (b) E. Ya. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements", Consultants Bureau, New York, 1966.
3. A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 87, 16 (1965).
4. L. H. Sommer, J. E. Lyons, and H. Fujimoto, J. Amer. Chem. Soc., 91, 7051 (1969).
5. S. Montelatici, A. van der Ent, J. A. Osborn,and G. Wilkinson, J. Chem. Soc. A, 1054 (1968).
6. For a review: R. E. Harmon, S. K. Gupta, and D. J. Brown, Chem. Revs., 73, 35 (1973).
7. (a) W. Fink, Helv. Chim. Acta, 54, 1304 and 2186 (1971);

(b) K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 28, C37 (1971).

8. (a) S. Takahashi, T. Shibano, and N. Hagihara, Chem. Commun., 161 (1969); (b) S. Takahashi, T. Shibano, H. Kojima, and N. Hagihara, Organometal. Chem. Syn., 1, 193 (1970/71); (c) H. Hara, K. Ohno, and J. Tsuji, Chem. Commun., 247 (1971).
9. (a) M.Kumada, Y. Kiso, and M. Umeno, Chem. Commun., 611 (1970); (b) Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, J. Organometal. Chem., 50, 297 (1973), and references therein; (c) B. W. Bennett and P. J. Orenski, J. Organometal. Chem., 28, 137 (1971).
10. (a) R. N. Haszeldine, R. V. Parish, and D. J. Parry, J. Chem. Soc. A, 683 (1969); (b) F. de Charentenay, J. A. Osborn, and G. Wilkinson, J. Chem. Soc. A, 787 (1968).
11. A. Panunzi and G. Paiaro, J. Amer. Chem. Soc., 88, 4843 (1966).
12. A. Smithies, M. Rycheck, and M. Orchin, J. Organometal. Chem., 12, 199 (1968).
13. J. Chatt and L. M. Venanzi, J. Chem. Soc., 2787 (1955).
14. (a) L. Horner and H. Winkler, Tetrahedron Lett., 461 (1964); (b) R. D. Baechler and K. Mislow, J. Amer. Chem. Soc., 92, 3090 (1970).
15. J. Chatt, N. P. Johnson, and B. L. Shaw, J. Chem. Soc., 1662 (1964).
16. There seems to be no racemization arising from dehydrosilylation of the adducts, since (*S*)-(+)-methylbutyltrichlorosilane does not racemize at all in the presence of chloroplatinic acid even at 180°: L. Spialter and D. H. O'Brien, J. Org. Chem., 31, 3048 (1966).
17. K. Yamamoto, Y. Uramoto, and M. Kumada, J. Organometal. Chem., 31, C9 (1971).
18. Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, J. Amer. Chem. Soc., 94, 4373 (1972).

19. J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Mo rrow, and C. Phillip, J. Amer. Chem. Soc., 93, 1301 (1971).
20. T. Hayashi, K. Yamamoto, and M. Kumada, unpublished results.
21. K. Yamamoto and M. Kumada, J. Organometal. Chem., 13, 131 (1968).
22. The ratio of two isomeric products thus obtained was in good accord with that reported by Speier and Musolf in the presence of chloroplatinic acid: M. C. Musolf and J. L. Speier, J. Org. Chem., 29, 2519 (1964).
23. K. I. Kobrakov, T. I. Chernysheva, and N. S. Nametkin, Dokl. Acad. Nauk, SSSR, 198, 1340 (1971) [Chem. Abstr., 75, 129908e (1971)].
24. R. J. Fessenden and W. D. Kray, J. Org. Chem., 38, 87 (1973); see also: H. Sakurai, T. Hirose, and A. Hosomi, 26th National Meeting of the Chemical Society of Japan, Abstr., 2E22 (1972).
25. K. Naumann, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 91, 7012 (1969).
26. The optical purity of (*R*)-benzylmethylphenylphosphine was determined by converting it into (*S*)-$[(PhCH_2)MePh\text{-}n\text{-}PrP]^+Br^-$, $[\alpha]_D^{22-24}$ +29.8° (*c* 1.20, MeOH); the maximum rotation reported for this compound is +36.8°. Mislow and coworkers[25] have reported the optical rotation of the tertiary phosphine with 95% optical purity, based on the same quaternization, to be +81°, but this figure seems to be too low.
27. L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, Tetrahedron Lett., 161 (1961).
28. J. W. Ryan and J. L. Speier, J. Org. Chem., 24, 2052 (1959).
29. E. A. Chernyshva and M. E. Dolgaya, Zhur. Obschei. Khim., 28, 2829 (1958).
30. J. Saam and J. L. Speier, J. Amer. Chem. Soc., 83, 1351 (1961).
31. A. D. Petrov and V. F. Mironov, Izv. Akad. Nauk, SSSR, 635

(1952).

32. A. V. Topchiev, N. S. Nametkin, and T. I. Chernysheva, Dokl. Akad. Nauk, SSSR, 115, 326 (1957).

33. S. P. Baksi and E. E. Turner, J. Chem. Soc., 171 (1961).

34. H. Pines and F. Schappell, J. Org. Chem., 29, 1503 (1964).

35. L. Lardicci, R. Rossi, S. Pussi, M. Aglietto, C. Botteghi, and P. Pino, Chim. Ind. (milan), 50, 227 (1968).

36. H. S. Mosher and E. La Combe, J. Amer. Chem. Soc., 72, 2829 (1950).

Chapter 3

Catalytic Asymmetric Hydrosilylation of Olefins. II. Chiral Phosphine-Nickel(II) Complex-catalyzed Reaction[1]

SUMMARY

Dichlorobis[(*R*)-benzylmethylphenylphosphine]nickel(II) was found to be a good catalyst precursor for the asymmetric hydrosilylation of 1,1-disubstituted prochiral olefins such as α-methylstyrene. The addition products were obtained in much higher optical yields than those using chiral platinum(II) complexes. Asymmetric induction was also observed in the hydrosilylation of 1,4-cyclohexadiene, which has a *meso* configuration upon coordination to the metal center. The stereochemical course of the asymmetric hydrosilylation of olefins is discussed in terms of mechanisms proposed for homogeneous catalytic hydrosilylation.

INTRODUCTION

In Chapter 2[2] intense studies on the catalytic asymmetric hydrosilylation of certain prochiral olefins have concentrated on seeking effective chiral platinum catalysts. It has been shown that dichlorobis(phosphine)di-μ-chlorodiplatinum(II) containing optically active tertiary phosphines as ligands is generally useful for a chiral catalyst precursor in asymmetric addition of methyldichlorosilane to 1,1-disubstituted olefins, though the extent of asymmetric induction is considerably low.

Since the potential catalytic activity of various phosphine-

complexes of nickel(II),[3] palladium(II),[3a,4] rhodium(I),[5] as well as platinum(II)[2] is now well documented in the literature, it seemed likely that asymmetric addition of a silicon hydride to certain olefins might be better achieved by use of one of these d^8 metal complexes having chiral phosphine ligands.

In the present chapter we describe that dichlorobis[(*R*)-benzylmethylphenylphosphine]nickel(II) (1) catalyzes the reaction with higher asymmetric bias than the platinum(II) system.

RESULTS AND DISCUSSION

Asymmetric hydrosilylation of 1,1-disubstituted olefins

Addition of methyldichlorosilane to α-methylstyrene (2a) was carried out in the presence of 1 in a degassed sealed glass tube at 90° for 60 hr, to give two types of addition products in 39% combined yield; one was the expected 2-phenylpropylmethyldichlorosilane (3a) as a major product and the other anomalous 2-phenylpropylmethylchlorosilane (4a), an addition product of methylchlorosilane, the latter arising from a nickel-catalyzed redistribution of methyldichlorosilane during the course of hydrosilylation (eq. 1). This SiH/SiCl interchange has extensively been examined by Kumada and coworkers[3c] with a variety of phosphine-nickel(II) complexes as hydrosilylation catalysts.

$$RMeC{=}CH_2 + HSiMeCl_2 \xrightarrow{Ni\text{-}\overset{*}{P}R_3} RMe\overset{*}{C}HCH_2SiMeCl_2 + RMe\overset{*}{C}HCH_2SiMeClH \quad (1)$$

2a, R = Ph — 3a-3c — 4a-4c
2b, R = *i*-Pr
2c, R = Et

$\overset{*}{P}R_3$ = (*R*)-(+)-($PhCH_2$)MePhP (BMPP) (81 or 67% optical purity)

By fractional distillation, 3a and 4a were obtained pure in optically active forms, having the almost identical degree of rotation (see Table I). 3a was converted into 2-phenylpropyltrimethylsilane (5), $[\alpha]_D^{15}$ +4.10° (neat), which was in 16.9% enantiomeric excess of the *R*-isomer, on the basis of a maximum rotation of (*R*)-(+)-5, $[\alpha]_D^{15}$ +24.3° (neat).[2] Taking account of an optical purity of the chiral phosphine used, the present asymmetric hydrosilylation proceeded with a 20.9% optical yield.

We have been unable to compare directly the catalytic activity of the phosphine complexes of nickel triad (Ni, Pd, and Pt), because neither platinum(II)[2] nor palladium(II) analog[6] of 1 has been found to be effective as a catalyst precursor for the addition of methyldichlorosilane to 2a.

However, the use of 1 with the same chiral phosphine as one used in the case of platinum(II) complexes resulted in giving much improved optical yields of the addition products. Although the exact structure of the catalytically active nickel species is uncertain, it is likely that the presence of two chiral phosphines per metal atom in the nickel complex is advantageous for asymmetric induction (20.9% optical yield) compared with the dichlorobis(phosphine)di-μ-chlorodiplatinum(II) (5.2% optical yield).[2]

It is also noteworthy that the two addition products obtained, 3a and 4a, have almost the same degree of optical rotation, despite the different addends, $MeCl_2SiH$ and $MeClSiH_2$. Although the latter would give rise to an asymmetric silicon atom in the resulting adduct 4a, the fact that an optically active dialkylchlorosilane readily racemizes[7] may apply to the extensive epimerization of 4a under the reaction conditions used. We did not pursue futher this point of view.

Asymmetric hydrosilylation of 2-methyl-1-butene (2c) and 2,3-dimethyl-1-butene (2b) was also carried out under the same conditions as described above. In every case, it was observed

Table I. Asymmetric Hydrosilylation of Olefins with $HSiMeCl_2$ Catalyzed by $Ni(\overset{*}{P}R_3)_2Cl_2$[a] (1) at 90°.

Olefin	Product	Yield (%)	$[\alpha]_D^{15}$, deg of product	$[\alpha]_D^{15}$, deg methylated	Optical yield (%)[b] (Configuration)
$PhMeC=CH_2$	$PhMeCHCH_2SiMeCl_2$	31	+6.50	+4.10	20.9 (*R*)
	$PhMeCHCH_2SiMeClH$	8	+6.43	—	
i-$PrMeC=CH_2$	*i*-$PrMeCHCH_2SiMeCl_2$	21[c]	-0.79	-1.00	6.2 (*R*)
	i-$PrMeCHCH_2SiMeClH$	26[c]	-0.90	—	
$EtMeC=CH_2$	$EtMeCHCH_2SiMeCl_2$	17[c]	—	-0.27	2.5 (*R*)
	$EtMeCHCH_2SiMeClH$	19[c]	-0.22		

[a] $\overset{*}{P}R_3$ = (*R*)-(+)-($PhCH_2$)MePhP (67% or 81% optical purity). [b] Based on the maximum rotation of authentic samples and calibrated for the optical purity of the chiral phosphine used. [c] Based on glc analysis.

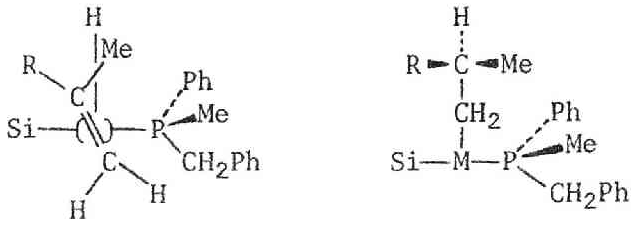
that the expected addition product (3b or 3c) was accompanied by comparable amount of another anomalous adduct (4b or 4c) which came from SiH/SiCl interchange of methyldichlorosilane (eq. 1).

All data obtained for asymmetric hydrosilylation of these 1,1-disubstituted olefins are summarized in Table I.

Although the nickel complex-catalyzed hydrosilylation of 2a-2c required higher temperature to give rather low reaction yield of addition products than the platinum system, as far as the asymmetric induction is concerned, the former always effected larger asymmetric bias onto the *R* configuration of the adducts than the latter. In addition, the extent of asymmetric induction was consistently in the order 2a > 2b > 2c in both cases.

The fact that (*R*)-benzylmethylphenylphosphine (BMPP) coordinated to the metal center can induce asymmetric addition of methyldichlorosilane across the carbon-carbon double bond of prochiral olefins may be explained in terms of the current views of mechanisms on metal-catalyzed hydrosilylation[8] where the following processes may be involved: (a) insertion of the metal center into the silicon-hydrogen bond; (b) addition of the resulting hydridometal moiety to the coordinated olefin preferentially from its *re* face (in a *cis* manner) to convert it into an alkyl-metal species; and (c) transfer of the silicon from the metal center to the alkylcarbon to afford the product. Since the process (b) most likely involves diastereomeric transition states or intermediates, the overall asymmetric bias onto the *R* configuration at the chiral carbon would have already been determined prior to the process (c). A schematic view of such a process is shown in the Scheme. On this basis it follows that different kinds of hydrosilanes may not significantly affect the optical yield of the addition reaction as mentioned above. In fact, this is also envisaged in rhodium(I) complex-catalyzed hydrosilylation, which will be described in Chapter 4.

Scheme



(R = Ph, *i*-Pr, Et; M = metal center)

Asymmetric hydrosilylation of other olefins

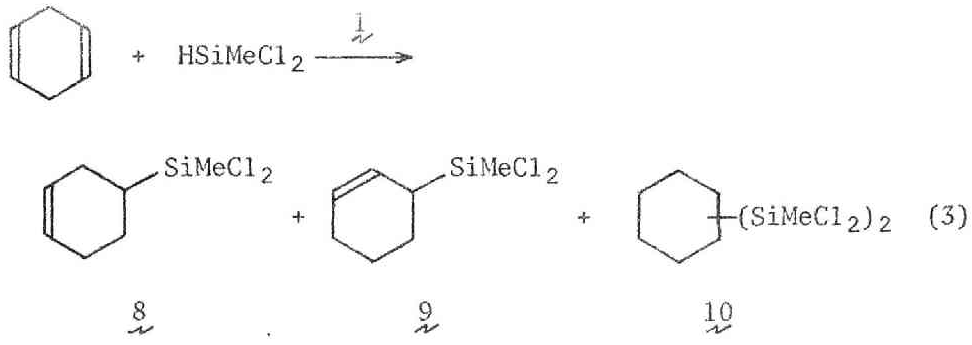
Two additional olefins, styrene and 1,4-cyclohexadiene, were also examined as to asymmetric hydrosilylation in the presence of 1, since a different mode of asymmetric induction from that discussed above seems to be operative for these olefins.

Addition of methyldichlorosilane to styrene catalyzed by 1 at 120° for 12 hr gave 1-phenylethylmethyldichlorosilane (6)[9] and isomeric 2-phenylethylmethyl derivative (7)[9] in 24% combined yield, and some polymeric substances. The glc area ratio of the two products was 46:54. No SiH/SiCl interchange as described above was observed in this case (eq. 2). The optical yield of

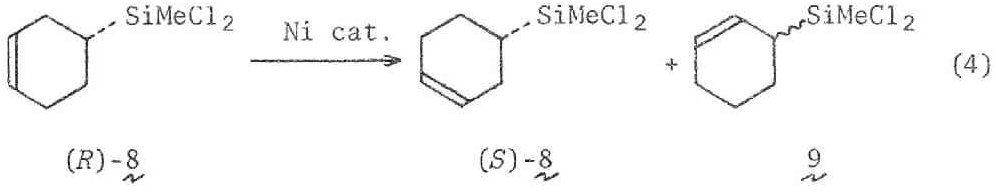
$$PhCH{=}CH_2 + HSiMeCl_2 \xrightarrow{1} \underset{6}{PhMe\overset{*}{C}HSiMeCl_2} + \underset{7}{PhCH_2CH_2SiMeCl_2} \qquad (2)$$

the product 6 was estimated to be 0.9% of the *R* isomer, on the basis of an empirical value of molecular rotations of 1-phenylethyl systems reported by Davis and Jensen.[10]

Of significance is the fact that hydrosilylation of 1,4-cyclohexadiene under the influence of 1 gave rise to some extent of asymmetric induction in one of three addition products.



Thus, addition of methyldichlorosilane to 1,4-cyclohexadiene was carried out in the presence of 1 at 90° for 40 hr, to give 4-(methyldichlorosilyl)cyclohexene (8) and 3-(methyldichlorosilyl)cyclohexene (9), in a ratio of 2.7:1, and bis(methyldichlorosilyl)cyclohexane (10) (eq. 3). The isomeric mixture of 8 and 9 was treated with methylmagnesium bromide and then by trifluoroacetic acid to give pure 4-trimethylsilylcyclohexene (11), $[\alpha]_D^{20}$ +3.69° (neat). On the basis of an empirical rule of conformational asymmetry of endocyclic olefinic compounds,[11] 11 was estimated to be at least of 4% enantiomeric purity with respect to the *R* isomer. It should be mentioned that the formation of 9 is attributed to an isomerization of 8 (*vide infra*) and that this isomerization inevitably results in some racemization of optically active 8 by a process shown in eq. 4.



Hydrosilylation of 1,3-cyclohexadiene under the same conditions did not appreciably occur, while at elevated temperature (120°) giving 8 and 9 in a ratio of 1:2.7. Therefore, the nickel

Table II. Hydrosilylation of 1,4- and 1,3-Cyclohexadiene Catalyzed by Chiral Phosphine Complexes of Nickel Triad.

Catalyst	Silane	Temp. (°C)	Time (hr)	Yield[a] (%)	Product ratio[b] 8	9	Optical activity
1,4-Cyclohexadiene							
Ni[c]	$HSiMeCl_2$	90	40	37	73	27	yes
Pd[d]	$HSiCl_3$	135	66	80	10[e]	90[e]	yes
Pt[f]	$HSiMeCl_2$	90	43	90	14	86	no
Pt[g]	$HSiMeCl_2$	90	28	83	nil	100	no
1,3-Cyclohexadiene							
Ni[c]	$HSiMeCl_2$	120	40	38	27	73	yes
Pd[d]	$HSiCl_3$	120	63	64	10	90	yes

[a] Combined yield of 8 and 9. [b] By glc analysis. [c] $Ni(\overset{*}{P}R_3)_2Cl_2$: $\overset{*}{P}R_3$ = (*R*)-$(PhCH_2)MePhP$. [d] $Pd(PhCN)_2Cl_2$ plus 2 MDPP: MDPP = (-)-Menthyldiphenylphosphine (see ref. 6). [e] Trichlorosilyl analog of 8 and 9, respectively. [f] *cis*-$(C_2H_4)\overset{*}{A}mPtCl_2$: $\overset{*}{A}m$ = (*S*)-$PhMeCHNH_2$. [g] *cis*-$(C_2H_4)R_3\overset{*}{P}PtCl_2$: $\overset{*}{P}R_3$ = (*R*)-$(PhCH_2)$-MePhP.

complex-catalyzed isomerization of 1,4-cyclohexadiene to the 1,3-isomer would be solw (and *vice versa*) under the present conditions. The isomeric mixture of 8 and 9, after methylation, had a slight optical activity (α_D^{20} -0.023° (0.1 dm, neat)). All results as well as those obtained with platinum catalysts for comparison are summarized in Table II.

In contrast to the use of a nickel catalyst, hydrosilylation of 1,4-cyclohexadiene catalyzed by *cis*-dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II) or its chiral phosphine analog readily took place to give 8 and 9 in 90% or 83% combined yield, respectively, but 9 was always predominant and optically inactive. Evidently, an extensive isomerization of the starting 1,4-diene to the 1,3-diene may precede the addition of methyldichlorosilane in this case.

Finally, when a *cis* olefin of C_{2v} symmetry is coordinated to the metal center, the two asymmetric carbon atoms formed have opposite configurations, yielding a *meso* compound.[12] Hence, the asymmetric induction for hydrosilylation of 1,4-cyclohexadiene should take place during and/or after formation of the diastereomeric alkyl-metal intermediates which arise from a stereoselective *cis* addition of hydridometal moiety to the coordinated *meso* diene. It may be, therefore, concluded that the asymmetric induction in the step of coordination of an olefin to the chiral complex catalyst is not necessarily an essential factor in order to sustain the asymmetric hydrosilylation in general.[13]

EXPERIMENTAL

Preparation of dichlorobis[(*R*)-benzylmethylphenylphosphine]-nickel(II) (1)

To a solution of 1.00 g (4.2 mmol) of nickel chloride hydrate in 15 ml of dry ethanol under an argon atmosphere was added

2.0 ml (8.8 mmol) of (*R*)-benzylmethylphenylphosphine (BMPP)[1] (67% optical purity) in one portion and the mixture was magnetically stirred overnight. The precipitates formed were taken up with methylene chloride. After removal of the solvent, the residue was recrystallized from CH_2Cl_2-petr. ether (1:5) to give 1.45 g (58%) of pure 1 as deep purple plates, mp 132-133° (in an evacuated tube). The optical rotation of this complex in methylene chloride could hardly be measured due to deeply red-colored solution. *Anal* Calcd for $C_{28}H_{30}Cl_2NiP_2$: C, 60.26; H, 5.42; Cl, 12.70. Found: C, 60.49; H, 5.64; Cl, 13.11.

The same complex but with the phosphine of 81% optical purity was also prepared.

Asymmetric hydrosilylation of 1,1-disubstituted olefins

The following procedure is typical: In a degassed sealed glass tube a mixture of an appropriate olefin (90 mmol), methyldichlorosilane (90 mmol) and the catalyst 1 (3.6×10^{-2} mmol) was heated at 90° for 60 hr. The reaction mixture was fractionally distilled to give two types of addition products. In some cases the product ratio was determined by glc analysis prior to distillation. The normal adduct (with no SiCl/SiH exchange) was then treated with excess methylmagnesium bromide to convert it into the trimethylsilyl derivative, with which the optical yield was determined on the basis of the maximum rotation of authentic samples.[2] All optical data are given in Table I.

1. α-Methylstyrene (2a). Using 1 with BMPP of 81% optical purity, two addition products, 2-phenylpropylmethyldichlorosilane (3a)[2] and 2-phenylpropylmethylchlorosilane (4a), were obtained by fractional distillation of the reaction mixture; 4a: bp 51-52° (0.8 mm), 1.4 g (8%) (95+% pure), n_D^{15} 1.5138, d_4^{15} 1.0119, nmr (CCl_4/TMS): δ 0.25 (d, *J* = 2.8 Hz, 3H, $SiCH_3$), 1.31 (d, *J* = 6.8 Hz, 2H, CH_2), 1.35 (d, *J* = 6.8 Hz, 3H, CCH_3), 3.04 (ill resolved m, 1H, CH), 4.67 (sextet, apparent *J* = 2.8 Hz, 1H, SiH), and 7.16

(s, 5H, C_6H_5). *Anal* Calcd for $C_{10}H_{15}ClSi$: C, 60.42; H, 7.61; Cl, 17.83. Found: C, 61.19; H, 7.59; Cl, 17.30. 3a: bp 66.0-66.5° (0.6 mm), 6.6 g (31%), n_D^{15} 1.5151, d_4^{15} 1.1110, (lit.[8] bp 148-149° (42 mm), n_D^{25} 1.5082, d_4^{25} 1.100). 3a was methylated to give 2-phenylpropyltrimethylsilane (5)[2], bp 100-100.5° (19 mm), n_D^{15} 1.4900, d_4^{15} 0.8681.

From another run of the same reaction but in 45 mmol-scale was obtained 4.4 g (42%) of the adducts, which gave, on direct methylation followed by preparative glc, pure 5; $[\alpha]_D^{15}$ +3.89° (neat). Taking account of an optical purity of the phosphine (81%), the optical yield of the addition product is 19.8%.

2. 2,3-Dimethyl-1-butene (2b). 1 with BMPP of 67% optical purity was used as catalyst. Simple distillation of the reaction mixture gave 8.2 g (47% combined yield) of two addition products, and the glc area ratio of the products was 56:44. The distillate was then fractionally redistilled to isolate each adduct in the pure state. (i) *i*-PrMeCHCH$_2$SiMeClH (4b), bp 64-66° (18 mm), 3.5 g, n_D^{20} 1.4354, d_4^{20} 0.8818, nmr(CCl_4/TMS): δ 0.47 (d, J = 3.2 Hz, SiCH_3), 4.83 (m, SiH), and other protons as diffused multiplets. Ir(liquid film): 2167 cm^{-1} (ν(Si-H)). *Anal* Calcd for $C_7H_{17}ClSi$: C, 51.03; H, 10.40; Cl, 21.52. Found: C, 50.44; H, 10.53; Cl, 20.01. (ii) *i*-PrMeCHCH$_2$SiMeCl$_2$[2] (3b), bp 74-76° (18 mm), 3.3 g, (97+% pure). Methylation of the adducts gave *i*-PrMeCHCH$_2$SiMe$_2$H, bp 70° (73 mm), n_D^{20} 1.4211, nmr(CCl_4/TMS): δ 0.13 (d, J = 3.4 Hz, SiCH_3), 3.97 (m, SiH), ir: 2124 cm^{-1} (ν(Si-H)). *Anal* Calcd for $C_8H_{20}Si$: C, 66.57; H, 13.97. Found: C, 66.75; H, 14.00., and *i*-PrMeCHCH$_2$SiMe$_3$[2], bp 96.5° (137 mm).

3. 2-Methyl-1-butene (2c). Similarly, simple distillation of the reaction mixture gave 7.5 g of addition products, which boiled over a range of 59-78° (32 mm) and consisted of four components. The glc area ratio of the products was 42:37:16:5. The major two were separated and identified as follows, while the other two could not be obtained pure.

The major adducts were: (i) $EtMeCHCH_2SiMeClH$ (4c), bp 43° (20 mm), n_D^{20} 1.4274, d_4^{20} 0.8813, nmr(CCl_4/TMS): δ 0.52 (d, J = 3.6 Hz, $SiCH_3$), 4.83 (m, SiH), and other protons as diffused multiplets, ir: 2172 cm^{-1} (ν(Si-H)). *Anal* Calcd for $C_6H_{15}ClSi$: C, 47.81; H, 10.03; Cl, 22.54. Found: C, 47.38; H, 10.36; Cl, 23.02. Methylation followed by preparative glc gave 2-methylbutyldimethylsilane, n_D^{20} 1.4151, nmr(CCl_4/TMS): δ 0.12(d, J = 3.9 Hz, $SiCH_3$) and 3.96 (m, SiH). *Anal* Calcd for $C_7H_{18}Si$: C, 64.52; H, 13.92. Found: C, 64.06; H, 14.06. (ii) $EtMeCHCH_2SiMeCl_2$[2] (3c), which was directly converted into trimethylsilyl derivative and purified by preparative glc. The optical rotations were as indicated in Table I.

Asymmetric hydrosilylation of styrene

A mixture of 18.8 g (0.18 mol) of freshly distilled styrene, 20.8 g (0.18 mol) of methyldichlorosilane and 40 mg (7×10^{-2} mmol) of 1 (with BMPP of 67% optical purity) was heated at 120° over a period of 12 hr. The reaction mixture was distilled to give 9.6 g (24% combined yield) of 1-phenylethyl- (6) and 2-phenylethylmethyldichlorosilane (7).[8] The glc area ratio of isomeric products was 46:54. The mixture was methylated. 1-Phenylethyltrimethylsilane was obtained by preparative glc in optically active form, $[\alpha]_D^{20}$ +0.62° (neat); $[M]_D^{20}$ +1.11°, 0.9% optical yield of the *R* isomer, which was estimated on the basis of the optical purity of the chiral phosphine used and of an empirical value of molecular rotation of (*S*)-(-)-1-phenylethyltrimethylsilane, $[M]_D^{20}$ -184° (± 5%).[9]

In another run of the same reaction catalyzed by 1 with BMPP of 81% optical purity, the optical rotation of 1-phenylethyltrimethylsilane was $[\alpha]_D^{20}$ +0.79° (*c* 6.09, benzene). With trichlorosilane the reaction did not take place under the conditions employed (*cf.* ref. 3b).

Asymmetric hydrosilylation of 1,4- and 1,3-cyclohexadiene

A mixture of 4.1 ml of 1,4-cyclohexadiene (containing 20% of benzene), 3.5 g (30 mmol) of methyldichlorosilane and 10 mg of 1 (81% optical pure BMPP) was heated at 90° for 40 hr. Fractional distillation of the reaction mixture gave two fractions: (i) bp 86-88° (16 mm), 2.1 ml, a mixture of 3- (8) and 2-cyclohexenylmethyldichlorosilane (9), α_D^{20} +0.691° (0.1 dm, neat); and (ii) bp 108-109° (3 mm), 0.9 ml, bis(methyldichlorosilyl)cyclohexane (10). Upon methylation of the first fraction was obtained trimethylsilyl derivatives of 8 and 9 in a ratio of 73:27, bp 62-63° (20 mm), 1.0 ml, α_D^{20} +0.492° (0.1 dm, neat).

A similar mixture (2.2 ml) of 4- and 3-trimethylsilylcyclohexene from another run was treated with trifluoroacetic acid (1.8 ml), and the mixture was distilled to give pure 4-trimethylsilylcyclohexene,[3c] bp 58-60° (17 mm), 0.9 ml, n_D^{20} 1.4580, d_4^{20} 0.8428, $[\alpha]_D^{20}$ +3.69° (neat); $[M]_D^{20}$ +5.68°, nmr: δ -0.05 (s, $SiCH_3$) and 5.64 (broad s, CH=CH). *Anal.* Calcd for $C_9H_{18}Si$: C, 70.05; H, 11.76. Found: C, 70.19; H, 11.62.

Similarly, from a mxture of 2.8 g (35 mmol) of 1,3-cyclohexadiene and 3.5 g (30 mmol) of methyldichlorosilane was obtained 8 (10%), 9 (28%), and 10 (10%). An isomeric mixture of 8 and 9, upon methylation, showed a slight negative rotation, α_D^{20} -0.023° (0.1 dm, neat). Furthermore, the similar reaction of 1,4-cyclohexadiene catalyzed by chiral platinum complexes (see Table II) yielded 8 and 9 in high yield, and there was no disilylated product. Neither of two isomeric products showed optical activity.

REFERENCES

1. A preliminary account of this work has appeared in J. Organometal. Chem., 31, C9 (1971).

2. K. Yamamoto, T. Hayashi, and M. Kumada, J. Amer. Chem. Soc., 93, 5301 (1971).
3. (a) S. Takahashi, T. Shibano, H. Kojima, and N. Hagihara, Organometal. Chem. Syn., 1, 193 (1970/71); (b) B. W. Bennett and P. J. Orenski, J. Organometal. Chem., 28, 137 (1971); (c) Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, J. Organometal. Chem., 50, 297 (1973), and references therein.
4. (a) S. Takahashi, T. Shibano, and N. Hagihara, Chem. Commun., 161 (1969); (b) M. Hara, K. Ohno, and J. Tsuji, Chem. Commun., 247 (1971).
5. (a) R. N. Haszerdine, R. V. Parish, and D. J. Parry, J. Organometal. Chem., 9, 31 (1967); J. Chem. Soc. A, 683 (1969); (b) F. de Charentenay, J. A. Osborn, and G. Wilkinson, J. Chem. Soc. A, 787 (1968).
6. Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, J. Amer. Chem. Soc., 94, 4373 (1972).
7. R. J. P. Corriu and G. F. Lanneau, Tetrahedron Lett., 2771 (1971).
8. C. Eaborn and B. W. Bott in A. G. MacDiarmid, Ed., "Organometallic Compounds of the Group IV Elements", Vol. 1. Part 1, Marcel Dekker, New York, N. Y., 1968, pp. 231-263.
9. J. W. Ryan and J. L. Speier, J. Org. Chem., 24, 2052 (1959).
10. D. D. Davis and F. R. Jensen, J. Org. Chem., 35, 3410 (1970).
11. J. H. Brewster, J. Amer. Chem. Soc., 81, 5493 (1959).
12. G. Paiaro, Organometal. Chem. Rev. A, 6, 319 (1970).
13. G. Consiglio, C. Botteghi, C. Salomon, and P. Pino, Angew. Chem., 85, 663 (1973).
14. K. Nauman, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 91, 7012 (1969).

Chapter 4

Catalytic Asymmetric Hydrosilylation of Olefins. III. Chiral Phosphine-Rhodium Complex-catalyzed Reaction

SUMMARY

In contrast to the platinum or nickel complex-catalyzed hydrosilylation of α-methylstyrene using methyldichlorosilane, the latter was of no use for the rhodium complexes as catalysts. Trimethylsilane and phenyldimethylsilane were found to add readily to α-methylstyrene in the presence of chiral rhodium complexes with (*R*)-benzylmethylphenylphosphine, or (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane to give optically active 2-phenylpropylsilane derivatives. The optical yields were not significantly affected by changes in structure of the hydrosilanes.

Hydrosilylation of styrene with trialkylsilanes catalyzed by the rhodium complex proceeded with high regioselectivity to form β-adduct.

INTRODUCTION

Among a variety of rhodium(I) complex-catalyzed reactions, hydrosilylation of olefins has attracted a little attention. Wilkinson *et al.*,[1] and Haszeldine *et al.*,[2] have independently reported the catalytic activity of chlorotris(triphenylphosphine)-rhodium(I) for the addition of various hydrosilanes to 1-hexene, while investigating the oxidative addition of silanes to this complex. More recently, several examples of the hydrosilylation

of terminal olefins and of acrylonitrile have also been reported.[3]

In the two preceding chapters, we have described that catalytic asymmetric hydrosilylation of prochiral olefins is realized by using chiral phosphine-platinum(II)[4] and -nickel(II)[5] complexes as catalysts. For instance, asymmetrically catalyzed addition of methyldichlorosilane to α-methylstyrene afforded (*R*)-2-phenylpropylmethyldichlorosilane in 5.2 and 20.9% optical yield, respectively.

We now extend these studies to include chiral rhodium complexes as catalysts for asymmetric hydrosilylation. In this work, we have found that changes in structure of hydrosilanes used do not significantly affect the extent of asymmetric induction.

RESULTS AND DISCUSSION

Asymmetric hydrosilylation of α-methylstyrene catalyzed by chiral rhodium complexes was carried out essentially as described in the preceding chapters. $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (1)[6] (S = solvent) and ((-)-DIOP)Rh(S)Cl (2),[7] where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane,[7] were used as catalysts for the present reactions. These complexes have been effectively used for asymmetric hydrogenation of olefins[7] and hydrosilylation of ketones.[6,8]

It should be mentioned that in the hydrosilylation of α-methylstyrene catalyzed by 1 or 2, methyldichlorosilane, which adds readily to several prochiral olefins in the presence of platinum(II)[4] and nickel(II)[5] complexes, scarcely reacted even under forced conditions. However, trialkylsilanes such as trimethylsilane and phenyldimethylsilane were found to be moderately reactive.

Table I. Asymmetric Hydrosilylation of α-Methylstyrene Catalyzed by Chiral Rhodium Complexes at 120° for 40 hr.

Silane	Catalyst[a]	Yield (%)	$[\alpha]_D^{20}$, deg[b] of product	Optical yield (%) (Configuration)
$HSiMe_3$	1	63	+1.19	7.0 (*R*)[c]
$HSiMe_2Ph$	1	25	+1.07	5.2 (*R*)[c]
$HSiMe_3$	2	63	-2.54	10.4 (*S*)
$HSiMe_2Ph$	2	19	-1.97	6.7 (*S*)

[a] Catalyst = 0.05 mol%. [b] Neat. [c] Calibrated for the optical purity of the chiral phosphine used (70%).

$$PhMeC{=}CH_2 + HSiMe_2R \xrightarrow[120^\circ]{1 \text{ or } 2} PhMe\overset{*}{C}HCH_2SiMe_2R \qquad (1)$$

3, R = Me

4, R = Ph

4 was converted into known compound 3 by way of a dimethylchlorosilyl derivative (5) in order to determine the enantiomeric excess (eq. 2).

$$\underset{4}{PhMe\overset{*}{C}HCH_2SiMe_2Ph} \xrightarrow[CHCl_3]{HCl\text{-}AlCl_3} \underset{5}{PhMe\overset{*}{C}HCH_2SiMe_2Cl} \xrightarrow{MeMgBr} \underset{3}{PhMe\overset{*}{C}HCH_2SiMe_3} \qquad (2)$$

The results obtained are summarized in Table I. It is of interest that changes in structure of hydrosilanes used do not significantly affect the extent of asymmetric induction in the rhodium complex-catalyzed hydrosilylation of α-methylstyrene.

It follows that the steric effect of a trialkylsilyl group bou to the rhodium catalyst on a stereochemical outcome for hydrosilylation of prochiral olefins should be a minor one compared to the steric control by the chiral phosphine-rhodium moiety which operates throughout the processes.[5] These arguments, in accord with the current views of mechanism of hydrosilylation, insist that the extent of asymmetric induction is already fixed in the process of forming diastereomeric alkyl-rhodium intermediates by way of the insertion of an olefin into a hydrido-rhodium moiety, rather than during the reductive elimination process where alkyl and trialkylsilyl groups both bound to the rhodium leave to form the final product (see Chapter 3).[5]

In addition, with respect to the effect of hydrosilanes upon the stereoselectivity, asymmetric hydrosilylation of olefins makes striking contrast with that of ketones where the optical yield varies dramatically with changes in structure of hydrosilanes employed, which will be described in Chapter 6.[6]

The addition reaction of trimethylsilane or phenyldimethylsilane to styrene in the presence of 1 resulted in giving exclusively the β-phenylethylsilyl derivatives, and the expected α-isomer was found only in a trace amount (eq. 3).

$$PhCH{=}CH_2 + HSiMe_2R \xrightarrow[110^\circ]{1} PhCH_2CH_2SiMe_2R \qquad (3)$$

6, R = Me
7, R = Ph

In contrast, with platinum(II)[4,9] or nickel(II)[5,10] the addition proceeds in two directions to afford both the α- and β-adduct in comparable amounts regardless of the use of various hydrosilanes, and only the α-adduct is formed in a trichlorosilane-palladium(II) system.[11]

EXPERIMENTAL

Asymmetric hydrosilylation of α-methylstyrene

The chiral cationic complex 1 was prepared *in situ* from $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (NBD = 2,5-norbornadiene) according to the reported procedure,[12] and the details are described in Chapter 6. A mixture of di-μ-chlorobis(1,5-hexadiene)-dirhodium and an equivalent of (-)-DIOP for the rhodium was used as catalyst 2.

1. With trimethylsilane. In 2.0 ml of degassed dry benzene and 0.4 ml of dichloromethane, 14 mg (2×10^{-2} mmol) of $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (with the phosphine of 70% optical purity) was dissolved, and molecular hydrogen was bubbled through the solution for 10 min. Then 4.7 g (40 mmol) of α-methylstyrene and 3.7 g (50 mmol) of trimethylsilane were added successively. The mixture was heated at 120° for 40 hr in a degassed sealed glass tube. Isolation of the product by preparative glc (Silicone DC550) after distillation (57° (4 mm)) gave 4.8 g (63%) of 2-phenylpropyltrimethylsilane (3),[4] $[\alpha]_D^{20}$ +1.19° (neat). Since the specific rotation of optically pure (*R*)-3 is $[\alpha]_D^{20}$ +24.3° (neat),[4] the enantiomeric excess of the product is 7.0% (*R*).

2. With phenyldimethylsilane. Similarly, a mixture of 7.1 g (60 mmol) of α-methylstyrene, 10.0 g (75 mmol) of phenyldimethylsilane was heated in the presence of 1 (3×10^{-2} mmol) at 120° for 40 hr to give 3.8 g (25%) of 2-phenylpropylphenyldimethylsilane (4), bp 132-134° (4 mm), n_D^{20} 1.5455, d_4^{20} 0.9630, $[\alpha]_D^{20}$ +1.07° (neat), nmr(CCl_4/TMS): δ 0.05 and 0.09 (a pair of s, $Si(CH_3)_2$), 1.16 (d, *J* = 6.6 Hz, CH_2), 1.22(d, *J* = 6.4 Hz, $CHCH_3$), 2.81 (sextet, CH), 7.11 (s, CC_6H_5), and 7.29 (broad s, SiC_6H_5). *Anal* Calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.71. Found: C, 79.61; H, 8.80.

4 was treated with dry hydrogen chloride in 15 ml of chloroform in the presence of a catalytic amount of aluminum chloride

to give 2.3 g (70%) of 2-phenylpropyldimethylchlorosilane (5), bp 73-75° (4 mm), n_D^{20} 1.5033, d_4^{20} 0.9899, $[\alpha]_D^{20}$ +1.47° (neat), nmr(CCl_4/TMS): δ 0.15 and 0.19 (a pair of s, $Si(CH_3)_2$), 1.12 (d, J = 7.2 Hz, CH_2), 1.30 (d, J = 7.2 Hz, $CHCH_3$), 3.01 (sextet, CH), and 7.19 (s, C_6H_5). *Anal* Calcd for $C_{11}H_{17}ClSi$: C, 62.09; H, 8.05; Cl, 16.66. Found: C, 62.27; H, 8.20; Cl, 16.01.

5 was methylated with excess methylmagnesium bromide in ether solution to obtain 3, $[\alpha]_D^{20}$ +0.88° (neat).

The results of asymmetric hydrosilylation of α-methylstyrene using 2 as catalyst are listed in Table I.

Hydrosilylation of styrene

1. With phenyldimethylsilane. A mixture of 5.2 g (50 mmol) of freshly distilled styrene, 7.5 g (55 mmol) of phenyldimethylsilane, and 2.5×10^{-2} mmol of 1 was heated at 110° for 7 days. The reaction mixture was distilled (bp 117-120° (2 mm)) to give 8.4 g (70%) of β-phenylethylphenyldimethylsilane (7), n_D^{20} 1.5502. Glc analysis indicated that only a trace amount of α-isomer is present. Nmr(CCl_4/TMS): δ 0.25 (s, 6H, $SiCH_3$), 0.96-1.32 (m, 2H, CH_2Si), 2.45-2.81 (m, 2H, $C_6H_5CH_2$), 7.09 (s, 5H, CC_6H_5), 7.0-7.6 (broad s, 5H, SiC_6H_5). *Anal* Calcd for $C_{16}H_{20}Si$: C, 79.93; H, 8.38. Found: C, 79.63; H, 8.33.

2. With trimethylsilane. From a mixture of 3.1 g (30 mmol) of styrene, 3.0 g (40 mmol) of trimethylsilane and 1.5×10^{-2} mmol of 1, was obtained 3.4 g (63%) of β-phenylethyltrimethylsilane (6), bp 100-102° (20 mm), n_D^{20} 1.4880, (lit.[9] bp 117° (40 mm), n_D^{25} 1.4840), nmr(CCl_4/TMS): δ 0.11 (s, $SiCH_3$), 0.81-1.03 (m, CH_2Si), 2.53-2.85 (m, $C_6H_5CH_2$), 7.15 (s, C_6H_5).

REFERENCES

1. F. de Charentenay, J. A. Osborn, and G. Wilkinson, J. Chem.

Soc. A, 787 (1968).

2. R. N. Haszeldine, R. V. Parish, and D. J. Parry, J. Chem. Soc. A, 683 (1969).
3. a) A. J. Chalk, J. Organometal. Chem., 21, 207 (1970); b) I. Ojima, M. Kumagai, and Y. Nagai, Tetrahedron Lett., 4005 (1974).
4. K. Yamamoto, T. Hayashi, M. Zembayashi, F. Sakurai, and M. Kumada, J. Org. Chem., to be submitted.
5. K. Yamamoto, T. Hayashi, Y. Uramoto, R. Ito, and M. Kumada, J. Org. Chem., to be submitted.
6. K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 54, C45 (1973).
7. T.-P. Dang and H. B. Kagan, Chem. Commun., 481 (1971); *idem*, J. Amer. Chem. Soc., 94, 6429 (1972).
8. a) W. Dumont, J.-C. Poulin, T.-P. Dang, and H. B. Kagan, J. Amer. Chem. Soc., 95, 8295 (1973); b) R. J. P. Corriu and J. J. E. Moreau, J. Organometal. Chem., 64, C51 (1974).
9. J. W. Ryan and J. L. Speier, J. Org. Chem., 24, 2052 (1959).
10. a) M. Kumada, Y. Kiso, and M. Umeno, Chem. Commun., 611 (1970); b) B. W. Bennett and P. J. Orenski, J. Organometal. Chem., 28, 137 (1971).
11. a) J. Tsuji, M. Hara, and K. Ohno, Tetrahedron, 30, 2143 (1974); b) Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, J. Amer. Chem. Soc., 94, 4347 (1972).
12. R. R. Schrock and J. A. Osborn, J. Amer. Chem. Soc., 93, 2397 (1971).

Chapter 5

Catalytic Asymmetric Hydrosilylation of Ketones. I. Chiral Phosphine-Platinum(II) Complex-catalyzed Hydrosilylation[1]

SUMMARY

Dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum(II) was found to be an effective catalyst for the hydrosilylation of alkyl phenyl ketones with methyldichlorosilane to give the corresponding silyl ethers of 1-phenylalkanols. In the case of dialkyl ketones, the reaction was accompanied considerably with the formation of silyl enol ethers.

Asymmetric hydrosilylation of a series of alkyl phenyl ketones catalyzed by chiral phosphine-platinum(II) complexes was undertaken. The products are readily converted into partially active 1-phenylalkanols.

INTRODUCTION

Although the homogeneous hydrogenation catalyzed by various transition metal complexes has been extensively studied[2] so far, it has been confined mostly to that of carbon-carbon multiple bonds. In regard to the hydrogenation of carbon-oxygen double bonds, there had been only a few papers[3] before Schrock and Osborn reported[4] in 1970 that cationic rhodium complexes with relatively basic phosphines as ligands catalyze the reduction of ketones under mild conditions. On the basis of these findings, a catalytic asymmetric hydrogenation of ketones has been achieved with a low optical yield.[5]

As for the hydrosilylation of carbonyl compounds, zinc

chloride[6] and chloroplatinic acid[7] were found to catalyze the reaction, even though of their limited applicability. Recently, Ojima and coworkers have reported[8] that chlorotris(triphenylphosphine)rhodium(I) is very effective for the hydrosilylation of carbonyl compounds. Corriu and Moreau have also studied[9] the addition of diarylsilanes to ketones in the presence of dichlorotris(triphenylphosphine)ruthenium(II) as well as the rhodium complex. The transition metal-catalyzed hydrosilylation of carbonyl compounds may be considered as a synthetically equivalent means to reduction.

In the preceding chapters, it has been shown that platinum(II),[10] nickel(II),[11] and rhodium(I)[12] complexes with chiral phosphines as ligands catalyze the enantioselective addition of hydrosilanes to prochiral olefins. With the aim at an asymmetric hydrosilylation of ketones, we have independently examined the behavior of several ketones toward addition of hydrosilanes in the presence of a variety of transition metal complexes with phosphine ligands. In this chapter, it is reported that the hydrosilylation of ketones with methyldichlorosilane proceeds under mild conditions by the use of $[(PhMe_2P)PtCl_2]_2$, and that one of its chiral phosphine analogs is useful for the asymmetric hydrosilylation of a series of alkyl phenyl ketones. Some chiral phosphine-rhodium complexes have also been found[13] to catalyze the reaction, with higher enantioselectivity than the platinum(II) system, which will be described in succeeding chapters.

RESULTS AND DISCUSSION

Hydrosilylation of ketones catalyzed by platinum(II) complexes

All experiments were carried out in degassed sealed glass tubes. In typical runs the catalyst concentration was about 10^{-3} mole per mole of a ketone and 1.3 equivalents of a hydrosilane

were used for each equivalent of a ketone. The mixture was allowed to stand at room temperature or heated, if necessary, for a given period of time. The addition products were isolated by distillation, and characterized by ir and nmr spectra and elemental analyses.

To begin with, various Group VIII transition metal complexes were examined in their catalytic activities for the addition reaction of methyldichlorosilane to acetophenone (eq. 1).

$$PhCOMe + HSiMeCl_2 \xrightarrow{\text{Catalyst}} PhMeCHOSiMeCl_2 \qquad (1)$$

Dichlorobis(phosphine)palladium(II) and -nickel(II) complexes exhibited no appreciable effect on the reaction even under forced conditions. Tris(triphenylphosphine)chlororhodium(I) also did not catalyze the hydrosilylation of acetophenone with methyldichlorosilane at all, though trialkylsilanes and dialkylsilanes were later found to enter into the reaction under mild conditions[8,9] (see Chapter 6). Platinum complexes seemed to be the only satisfactory catalysts for the reaction of methyldichlorosilane with acetophenone, so that several phosphine-platinum complexes as catalysts were examined in some detail. The yield of the silyl ether of 1-phenylethanol varied markedly depending on the nature of the catalyst used. As shown in Table I, it is noted that dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum(II) (1) was the most effective catalyst, whereas its triphenylphosphine analog had little catalytic activity. In accord with the nature of cationic rhodium complexes with more basic phosphines, these facts may suggest that a relatively electron-donating phosphine ligand plays an important role in facilitating the coordination of a carbonyl moiety to the coordinatively unsaturated platinum complex and, as a result, giving

Table I. Hydrosilylation of Acetophenone with Methyldichlorosilane Catalyzed by Transition Metal Complexes.

Catalyst	Condition		Yield[a]
	Temp (°C)	Time (hr)	(%)
H_2PtCl_6	r.t.	250	33
cis-$(C_2H_4)Am^*PtCl_2$[b]	r.t.	40	51
cis-$(R_3P^*)_2PtCl_2$[c]	r.t.	90	3
$[(PhMe_2P)PtCl_2]_2$	r.t.	40	80
$[(Ph_3P)PtCl_2]_2$	r.t.	60	4
$(PhMe_2P)_2PdCl_2$	120	40	0
$[(PhMe_2P)PdCl_2]_2$	120	40	0
trans-$(R_3P^*)_2NiCl_2$[c]	90	20	0
$(Ph_3P)_3RhCl$	50	40	0

[a] Yields were determined by glc based on acetophenone used.
[b] Am*: (*S*)-$PhMeCHNH_2$. [c] R_3P^*: (*R*)-$(PhCH_2)MePhP$.

rise to the addition of methyldichlorosilane to the ketone. Dichlorobis(phosphine)platinum(II) was of no use as a catalyst precursor for the hydrosilylation of ketones, nor for that of prochiral olefins.[10]

The addition of other hydrosilanes such as dialkyl- and trialkylsilanes to acetophenone catalyzed by 1 was carried out (eq. 2). The ease with which the addition reaction occurred was dependent strongly on the nature of silanes employed: methylphenylsilane added readily to the ketone at room temperature to

$$PhCOMe + HSiR_3 \xrightarrow[\text{r.t. 40 hr}]{1} PhMeCHOSiR_3 \qquad (2)$$

give the corresponding silyl ether in 80% yield. Phenylsilane also added, the major product being not a 1:1 adduct of phenylsilane but 1:2 adduct. On the other hand, trimethylsilane, dimethylphenylsilane, diethoxymethylsilane, and dichlorophenylsilane did not react at all so far as the platinum(II) catalyst 1 was used.

The hydrosilylation of a few dialkyl ketones with methyldichlorosilane gave rather complicated results, always being accompanied by the formation of silyl enol ethers[14] as indicated in the following equations.

$$EtCOMe + HSiMeCl_2 \xrightarrow[r.t.]{1} EtMeCHOSiMeCl_2 + \underset{(3\%)}{\overset{Me}{\overset{H}{>C=C<}}\!\!\begin{matrix}Me\\OSiMeCl_2\end{matrix}} + \underset{(2\%)}{\overset{Me}{\overset{H}{>C=C<}}\!\!\begin{matrix}OSiMeCl_2\\Me\end{matrix}} \quad (3)$$

(31%)

$$t\text{-}BuCOMe + HSiMeCl_2 \xrightarrow[r.t.]{1} t\text{-}BuMeCHOSiMeCl_2 + \underset{(4\%)}{\overset{t\text{-}Bu}{\overset{MeCl_2SiO}{>C=CH_2}}} \quad (4)$$

(9%)

$$PhCH_2COMe + HSiMeCl_2 \xrightarrow[r.t.]{1} PhCH_2MeCHOSiMeCl_2 + \underset{(8\%)}{\overset{Ph}{\overset{H}{>C=C<}}\!\!\begin{matrix}Me\\OSiMeCl_2\end{matrix}} + \underset{(3\%)}{\overset{Ph}{\overset{H}{>C=C<}}\!\!\begin{matrix}OSiMeCl_2\\Me\end{matrix}} \quad (5)$$

(29%)

Since the formation of silyl enol ethers should take place with concomitant evolution of hydrogen, it is conceivably possible to argue that the silyl ethers of alkanols might arise from some catalytic hydrogenation of silyl enol ethers initially formed. However, attempted hydrogenation of α-trimethylsiloxystyrene gave no appreciable amount of the silyl ether of 1-phenylethanol under the same conditions as mentioned above, so that the possibility *via* silyl enol ethers may be ruled out. The formation of silyl enol ethers in the presence of platinum complex 1 and the catalytic hydrosilylation of ketones are most likely competing processes. As to the mechanism for the formation of silyl enol ethers, there exist at least two possibilities on the basis of known homogeneous catalyses; (a) a pathway involving dehydrogenative condensation[15] between hydrosilane and enol present in equilibrium with ketone, and (b) one involving the well-recognized β-elimination of platinum-hydride from an α-siloxyalkylplatinum intermediate, which, if not isolated, would be formed *via* migration of the silyl ligand from metal to coordinated carbonyl oxygen atom. Although, at present, these two alternatives can not be differentiated, the authors are inclined to believe that the latter pathway may be of significance when more substituted silyl enol ethers are exclusively formed.

Asymmetric hydrosilylation of ketones catalyzed by chiral phosphine-platinum complexes

Dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum(II) (1) is found to be a specifically effective catalyst for hydrosilylation of alkyl phenyl ketones as mentioned above. Accordingly, dichlorobis[(*R*)-benzylmethylphenylphosphine]di-μ-chlorodiplatinum(II) (2)[10] or its (*R*)-methylphenyl-*n*-propylphosphine analog (3)[10] would be suitable for the asymmetric hydrosilylation of the prochiral ketones. Indeed, the addition of methyldichlorosilane to a series of alkyl phenyl ketones catalyzed by these

chiral phosphine-platinum(II) complexes gave partially active silyl ethers of 1-phenylalkanols, and the silyl ethers were readily converted into the corresponding 1-phenylalkanols by treating with methyllithium as in eq. 6.

$$\mathrm{PhCOR} + \mathrm{HSiMeCl_2} \xrightarrow{[\mathrm{L^*PtCl_2}]_2} \mathrm{PhR^*CHOSiMeCl_2} \xrightarrow[2)\ \mathrm{H_3O^+}]{1)\ \mathrm{MeLi}} \mathrm{PhR^*CHOH} \qquad (6)$$

(R = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu, *t*-Bu; L* = chiral phosphine)

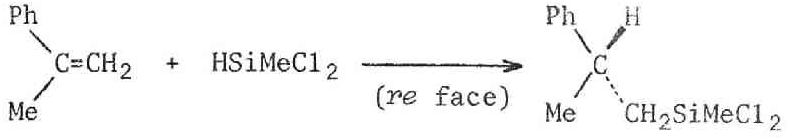
The results for a series of alkyl phenyl ketones examined are summarized in Table II. It is noteworthy that the platinum(II) complex 2 catalyzes the asymmetric addition of methyldichlorosilane to the ketones leading predominantly to (*S*)-1-phenylalkanols, whereas 3 to the (*R*)-enantiomers except for pivalophenone.

The results clearly indicate that, in the two phosphines employed, it is the only chiral nature at the phosphorus atom to be transmitted in the diastereomeric transition states that is opposite. This is not the case for the asymmetric hydrosilylation of, for example, α-methylstyrene with methyldichlorosilane.[10] Furthermore, the latter reaction catalyzed by 2 gives rise to the (*R*)-adduct predominantly, while (*S*)-1-phenylethanol is the preferred enantiomer in the case of asymmetric addition of methyldichlorosilane to acetophenone as given in Table II. These facts may well imply that the stereoselectivity for the addition of a hydrosilane to the enantiotopic faces of a ketone is different from that of an olefin which is undoubtedly in π-coordination to the chiral catalyst (see eq. 7 and 8).

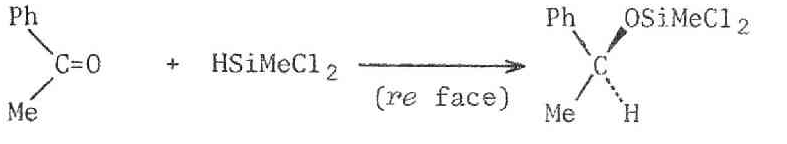
Table II. Asymmetric Hydrosilylation of RCOPh with $HSiMeCl_2$ Catalyzed by $[L^*PtCl_2]_2$ at Room Temperature.[a]

R	Yield (%)	Silyl ether[b] $[\alpha]_D^{20}$ (neat)	Carbinol[b] $[\alpha]_D^{20}$	Optical yield (%)[c] (Configuration)
L*: (*R*)-(+)-($PhCH_2$)MePhP (79% optical purity)				
Me	81	-4.60	-2.61	7.6 (*S*)
Et	81	-6.11	-2.21	10.0 (*S*)
n-Pr	77	-5.21	-3.0[d]	8.4 (*S*)
i-Pr	55[e]	—	-1.7[f]	4.5 (*S*)
i-Bu	65	—	-4.74[g]	18.6 (*S*)
t-Bu[h]	33	-6.74	-3.8[i]	18.6 (*S*)
L*: (*R*)-(-)-MePh-*n*-PrP (93% optical purity)				
Me	71	+3.81	+2.24	5.5 (*R*)
Et	83	+5.13	+1.94	7.4 (*R*)
n-Pr	74	+3.82	+2.0[d]	4.7 (*R*)
i-Pr	57[e]	—	+1.1[f]	2.5 (*R*)
i-Bu	54	—	+0.03[g]	0.1 (*R*)
t-Bu[h]	24	-2.62	-1.5[i]	6.2 (*S*)

[a] $[L^*PtCl_2]_2 = 6.7\times10^{-2}$mol%. [b] Specific rotation was measured neat unless otherwise noted. [c] Optical yields are calculated from the specific rotation of the pure enantiomers which are reported in the literature (lit. 16), and calibrated for the optical purity of chiral phosphines used. [d] Specific rotation in benzene; maximum rotation $[\alpha]_D^{27}$ -45.9° (*c* 6, benzene) (lit. 17). [e] Contaminated with *ca.* 10% of $Ph(MeCl_2SiO)C{=}CMe$. [f] Specific rotation in ether. [g] Specific rotation in *n*-heptane. [h] Heated at 90° for 10 days. [i] Specific rotation in benzene.

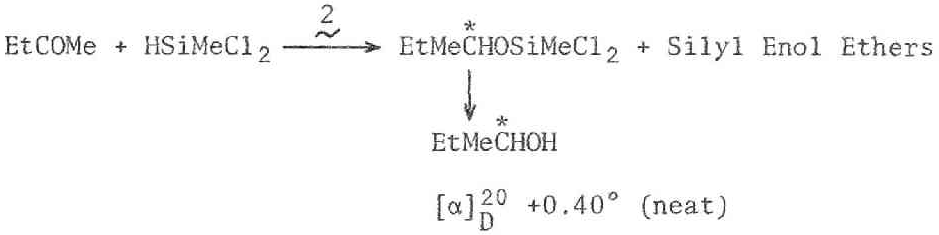


(5.2% o.y., *R*) (7)



(7.6% o.y., *S*) (8)

An asymmetric induction was also observed in hydrosilylation of 2-butanone, but the optical yield was only 3.6% of the *S* configuration as shown in equation 9.



$[\alpha]_D^{20}$ +0.40° (neat) (9)

The addition of methylphenylsilane to acetophenone and to pivalophenone in the presence of 2 was also carried out, and the results are shown in Table III. The optical purity of the resulting alcohol was much lower in both cases than that with methyldichlorosilane. The marked dependence of the extent of asymmetric induction on the structure of hydrosilanes employed, which seems to be notable in chiral phosphine-rhodium system, will be fully discussed in Chapter 6.[13a]

Instead of chiral tertiary phosphine-platinum complexes, using *cis*-dichloro(ethylene)[(*S*)-1-phenylethylamine]platinum(II)[18] as a catalyst, the adduct was obtained in very low optical purity;

Table III. Asymmetric Hydrosilylation of RCOPh with H_2SiMe_2 Catalyzed by $[\{(R)\text{-}(PhCH_2)MePhP\}PtCl_2]_2$ (2) at Room Temperature.[a]

R	Yield (%)	Silyl ether[b] α_D^{20} (0.1 dm, neat)	Carbinol $[\alpha]_D^{20}$ (neat)	Optical yield (%) (Configuration)	
Me	90	-0.204	-1.32	3.8	(*S*)
t-Bu	59	+0.020	+0.15[c]	0.7	(*R*)

[a] 2 = 6.7×10^{-2} mol%. [b] A mixture of two diastereomeric isomers. [c] Specific rotation in benzene.

for example, the silyl ether from acetophenone and methyldichlorosilane had $[\alpha]_D^{20}$ +0.34°.

Although optical yields obtained are rather low in the present platinum(II) catalyst system compared with a cationic rhodium complex[13a] of the same chiral phosphine as one used here, the fact that the platinum complexes contain only one chiral phosphine molecule allows one to discuss a simple correlation of given chiral information with the stereoselective addition to enantiotopic faces of the substrate.

EXPERIMENTAL

General comments

All boiling points described here are uncorrected. The ^1H nmr spectra were obtained on a Varian T-60 or HA-100 spectrometer in carbon tetrachloride solution containing TMS as an internal standard. Infrared spectra were measured on a Hitachi ERI-G3 grating spectrometer. A Varian Aerograph Model 90P, equipped with a 20 ft. column packed with Apiezon-L (30% on Celite) or

Silicone DC550 (30% on Celite), was used, if necessary, for isolation and purification of products. The optical rotations were measured with a Yanagimoto OR-50 polarimeter.

The preparation of metal complexes with chiral ligands was described in preceding chapters, and other phosphine complexes were prepared by the literature methods: $[(PhMe_2P)PtCl_2]_2$,[19] $[(Ph_3P)PtCl_2]_2$,[20] and $[(PhMe_2P)PdCl_2]_2$.[19]

Hydrosilylation of acetophenone with methyldichlorosilane catalyzed by some transition metal complexes

All reactions were carried out by the following procedures. In a degassed sealed glass tube a mixture of acetophenone (1 part), methyldichlorosilane (1.3 parts), and a catalyst (0.7×10^{-3} part) was heated for a given period of time. 1-Phenylethyl methyldichlorosilyl ether (4) was isolated by fractional distillation. The ^1H nmr, physical constants, and analytical data of 4 were listed in Tables IV and V. The yield in each case was generally determined by glc, and the results obtained for hydrosilylation of acetophenone with methyldichlorosilane are summarized in Table I.

The reaction with other hydrosilanes was carried out in the same way as in the case with methyldichlorosilane.

Hydrosilylation of dialkyl ketones with methyldichlorosilane

1. 2-Butanone. A mixture of 4.3 g (60 mmol) of 2-butanone, 9.2 g (80 mmol) of methyldichlorosilane, and 16 mg (4×10^{-2} mmol) of dichlorobis(dimethylphenylphosphine)di-μ-chlorodiplatinum (1) was allowed to stand at room temperature over a period of 40 hr to give by distillation (60-64° (50 mm)) 4.0 g (36% combined yield) of the mixture of three products, which were hardly isolated. However, on the basis of nmr analysis, this consisted of *sec*-butyl methyldichlorosilyl ether (5) and (*Z*)- and (*E*)-2-methyldichlorosiloxybut-2-ene (6) in a ratio of 31:3:2. Nmr: 5; δ

0.77 (s, $SiCH_3$), 0.93 (t, J = 6.6 Hz, CH_2CH_3), 1.27 (d, J = 6.0 Hz, $CHCH_3$), 1.50 (q, J = 6.4 Hz, CH_2CH_3), and 4.20 (sextet, OCH). (Z)-6; δ 0.82 (s, $SiCH_3$), 1.58 (double q, J = 1.0 and 7.2 Hz, $=CHCH_3$), 1.82 (overlapping q, $OCCH_3$), and 4.98 (q of q, J = 1.0 and 6.8 Hz, $=CH$). (E)-6; δ 1.52 (double q, ill resolved, $CHCH_3$), 1.89 (broad s, $OCCH_3$), and 4.62 (diffused q, $=CH$).

2. 3,3-Dimethyl-2-butanone. From a mixture of 6.0 g (60 mmol) of 3,3-dimethyl-2-butanone, 9.2 g (80 mmol) of methyldichlorosilane, and 16 mg (4×10^{-2} mmol) of 1 was obtained 1.7 g (13% combined yield)of the mixture of 2-methyldichlorosiloxy-3,3-dimethylbutane (7) and 2-methyldichlorosiloxy-3,3-dimethylbut-1-ene (8): bp 73-77° (44 mm), nmr: 7; δ 0.76 (s, $SiCH_3$), 0.91 (s, $C(CH_3)_3$), 1.21 (d, J = 6.2 Hz, $CHCH_3$), and 3.94 (q, OCH). 8; δ 0.86 (s, $SiCH_3$), 1.11 (s, $C(CH_3)_3$), and 4.37 (AB, J = 2.0 Hz, $\Delta\nu$ = 3.6 Hz, $=CH_2$).

3. 1-Phenyl-2-propanone. Similarly, by fractional distillation over a range of 79-86° (4 mm) of the reaction mixture, 1-phenyl-2-methyldichlorosiloxypropane (9) and (Z)- and (E)-1-phenyl-2-methyldichlorosiloxypropene (10) were obtained in 40% combined yield. Nmr: 9; δ 0.64 (s, $SiCH_3$), 1.27 (d, J = 6.0 Hz, $CHCH_3$), 2.71-2.88(double d, CH_2), 4.43 (sextet, J = 6.2 Hz, OCH), and 7.19 (S, C_6H_5). (Z)-10; δ 0.97 (s, $SiCH_3$), 2.05 (s, $=CCH_3$), 6.09-6.17 (broad s, $=CH$), and 7.15 (broad s, C_6H_5). (E)-10; δ 0.80 (s, $SiCH_3$), 2.14 (s, $=CCH_3$), 5.52-5.60 (broad s, $=CH$), and 7.15 (broad s, C_6H_5).

The ratio of these compounds thus obtained is shown in the text.

Asymmetric hydrosilylation of ketones with methyldichlorosilane

1. Alkyl phenyl ketones. The reaction conditions, yields, and optical data of the products are summarized in Table II. Some physical constants, analytical data, and ^1H nmr spectra for the silyl ethers are listed in Tables IV and V. The following

procedure for an asymmetric hydrosilylation of acetophenone is typical. Under a nitrogen atmosphere 9.2 g (80 mmol) of methyldichlorosilane was added to 7.2 g (60 mmol) of acetophenone in the presence of 20 mg (4×10^{-2} mmol) of 2 (with phosphine of 79% optical purity). The reaction mixture was stirred at room temperature over a period of 40 hr. The product was isolated by distillation through a short Vigreux column to give 11.4 g (81% yield) of 1-phenylethyl methyldichlorosilyl ether (4), bp 109° (18 mm), $[\alpha]_D^{20}$ -4.60° (neat).

To the adduct thus obtained was added dropwise excess methyllithium in ether solution under stirring at 0°. After 2 hr reflux, the reaction mixture was hydrolyzed with dilute hydrochloric acid. The organic products were extracted with ether and this ether extract was dried over sodium sulfate. After evaporation of ether, distillation under reduced pressure gave almost quantitatively 1-phenylethanol, $[\alpha]_D^{20}$ -2.61° (neat), (lit.[16] maximum rotation $[\alpha]_D^{21}$ -43.5 (neat)). Considering an optical purity of the phosphine (79%), the optical yield of the addition product is 7.6%. The alcohol was identified by comparison of the glc retention time and the nmr spectra with those of an authentic sample.

The reaction of isobutyrophenone with methyldichlorosilane catalyzed by 2 or 3 was accompanied by the formation of *ca.* 10% of 2-methyl-1-methyldichlorosiloxy-1-phenylpropene, nmr: δ 0.63 (s, $SiCH_3$), 1.74 and 1.86 (a pair of s, $C(CH_3)_2$), and 7.32 (s, C_6H_5).

2. 2-Butanone. From a mixture of 8.8 g (120 mmol) of 2-butanone, 18.4 g (160 mmol) of methyldichlorosilane, and 39 mg (8×10^{-2} mmol) of 2 was obtained 7.5 g (39% combined yield) of the mixture of *sec*-butyl methyldichlorosilyl ether and silyl enol ethers in the same proportion as described above, α_D^{20} +0.055° (0.1 dm, neat). The adducts were treated with excess methyllith-

Table IV. Physical Constants and Analytical Data for Hydrosilylation Products.

Compound	Bp (°C/mm)	n_D^{20}	d_4^{20}	C% Found (Calcd)	H% Found (Calcd)	Cl% Found (Calcd)
$RPhCHOSiMeCl_2$						
R = Me	97/17	1.4920	1.1464	46.43 (45.96)	5.12 (5.14)	29.89 (30.15)
R = Et	124/22	1.4910	1.1251	48.40 (48.20)	5.80 (5.66)	28.38 (28.45)
R = *n*-Pr	79/3	1.4888	1.1022	50.45 (50.19)	6.39 (6.13)	26.66 (26.49)
R = *t*-Bu	77/2	1.4904	1.0831	53.02 (51.98)	6.76 (6.54)	25.43 (25.57)
RPhCHOSiHMePh[a]						
R = Me	107-11/3	—	—	73.98 (74.32)	7.62 (7.48)	
R = *t*-Bu	120-37/3	—	—	75.75 (76.00)	8.80 (8.50)	

[a] A mixture of diastereoisomers.

ium in ether solution and then hydrolyzed to give after preparative glc 2-butanol, $[\alpha]_D^{20}$ +0.40° (neat), (lit.[21] maximum rotation, $[\alpha]_D^{20}$ +13.83° (neat)).

Asymmetric hydrosilylation of acetophenone and pivalophenone with methylphenylsilane

The procedure for the reaction with methyldichlorosilane was followed except that 9.0 g (75 mmol) of methylphenylsilane was used. Yields and optical data are summarized in Table III.

Table V. ^{1}H Nmr Data for RPhCHOSiMeCl$_2$.

R	Chemical shifts (δ)[a]		
	SiC*H*$_3$	OC*H*	Others[b]
Me	0.76(s)	5.25(q, J = 6.4 Hz)	1.56(d, J = 6.4 Hz, C*H*$_3$)
Et	0.71(s)	4.98(t, J = 6.3 Hz)	0.89(t, J = 7.0 Hz, C*H*$_3$)
			1.61-2.11(m, C*H*$_2$)
n-Pr	0.71(s)	5.05(t, J = 6.3 Hz)	0.92(t, J = 7.2 Hz, C*H*$_3$)
			0.9-2.4(m, C*H*$_2$C*H*$_2$)
i-Pr	0.69(s)	4.73(d, J = 6.2 Hz)	0.81 and 0.96(a pair of
			d, J = 6.4 Hz, 2C*H*$_3$)
			1.95(sep, J = 6.4 Hz, C*H*)
i-Bu	0.68(s)	5.12(t, J = 6.2 Hz)	0.95(d, J = 6.0 Hz, 2C*H*$_3$)
			0.8-2.6(m, C*H*$_2$C*H*)
t-Bu	0.68(s)	4.71(s)	0.94(s, C(C*H*$_3$)$_3$)

[a] Carbon tetrachloride solution with tetramethylsilane as an internal standard; s singlet, d doublet, t triplet, q quartet, sep septet, m multiplet. [b] The chemical shift for phenyl protons is 7.23-7.29 ppm (s).

The silyl ether was obtained as a mixture of two diastereoisomers. Glc and nmr analyses indicated that the diastereoisomers were formed in nearly equal amounts in both cases. Boiling points and analytical data of silyl ethers are shown in Table IV. ^{1}H nmr(CCl$_4$/TMS): PhMeCHOSiHMePh; δ 0.34 and 0.37 (d, J = 2.9 Hz, SiC*H*$_3$), 1.40 and 1.43 (d, J = 6.3 Hz, CHC*H*$_3$), 4.81 (q, OC*H*), 4.93 and 5.02 (q, Si*H*), 7.12 and 7.20 (s, CC$_6$*H*$_5$), and 7.06-7.57 (m, SiC$_6$*H*$_5$). *t*-BuPhCHOSiHMePh; δ 0.23 and 0.31 (d, J =2.9 Hz, SiC*H*$_3$), 0.85 and 0.86 (s, CC*H*$_3$), 4.26 (s, OC*H*), 4.86 and 4.92 (q, Si*H*), 7.14 and 7.18 (s, CC$_6$*H*$_5$), and 7.06-7.54 (m, SiC$_6$*H*$_5$).

1. A preliminary communication has appeared in J. Organometal. Chem., 46, C65 (1972).
2. For reviews: a) B. R. James, "Homogeneous Hydrogenation", Wiley Interscience, New York, 1973. b) R. E. Harmon, S. K. Gupta, and D. J. Brown, Chem. Revs., 73, 35 (1973).
3. H. B. Henbest and T. R. B. Mitchell, J. Chem. Soc. C, 785 (1970).
4. R. R. Schrock and J. A. Osborn, Chem. Commun., 567 (1970).
5. P. Bonvicini, A. Levi, G. Modena, and G. Scorrano, J. C. S. Chem. Commun., 1188 (1972).
6. R. Calas, E. Frainnet, and J. Bonastre, C. R. Acad. Sci. Paris, 251, 2987 (1960).
7. S. I. Sadykh-Zade and A. D. Petrov, Zh. Obshch. Khim., 29, 3194 (1959).
8. a) I. Ojima, M. Nihonyanagi, and Y. Nagai, J. C. S. Chem. Commun., 938 (1972). b) I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, Bull. Chem. Soc. Japan, 45, 3506 (1972).
9. R. J. P. Corriu and J. J. E. Moreau, J. C. S. Chem. Commun., 38 (1973).
10. K. Yamamoto, T. Hayashi, and M. Kumada, J. Amer. Chem. Soc., 93, 5301 (1971); K. Yamamoto, T. Hayashi, M. Zembayashi, F. Sakurai, and M. Kumada, J. Org. Chem., to be submitted.
11. K. Yamamoto, Y. Uramoto, and M. Kumada, J. Organometal. Chem., 31, C9 (1971); K. Yamamoto, T. Hayashi, Y. Uramoto, R. Ito, and M. Kumada, J. Org. Chem., to be submitted.
12. T. Hayashi, K. Yamamoto, and M. Kumada, J. Org. Chem., to be submitted.
13. a) K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 54, C45 (1973); T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 4405 (1974). b) I. Ojima, T. Kogure, and Y. Nagai, Chem. Lett., 541 (1973); I. Ojima and Y. Nagai,

Chem. Lett., 223 (1974). c) W. Dumont, J.-C. Poulin, T.-P. Dang, and H. B. Kagan, J. Amer. Chem. Soc., 95, 8295 (1973). d) R. J. P. Corriu and J. J. E. Moreau, J. Organometal. Chem., 64, C51 (1974).

14. Y. Nagai, K. Uetake, T. Yoshikawa, and H. Matsumoto, Yuki Gosei Kagaku Kyokai Shi, 31, 759 (1973), and the references cited therein.
15. L. H. Sommer and J. E. Lyons, J. Amer. Chem. Soc., 91, 7061 (1969), and the references cited therein.
16. R. McLeod, F. J. Welch, and H. S. Mosher, J. Amer. Chem. Soc., 82, 876 (1960).
17. K. Mislow and C. L. Hamermesh, J. Amer. Chem. Soc., 77, 1950 (1955).
18. A. Panunzi and G. Paiaro, J. Amer. Chem. Soc., 88, 4843 (1966).
19. J. M. Jenkins and B. L. Shaw, J. Chem. Soc. A, 770 (1966).
20. R. J. Goodfellow and L. M. Venanzi, J. Chem. Soc., 1072 (1965).
21. J. Kenyon, H. Phillips, and V. P. Pittman, J. Chem. Soc., 1072 (1935).

Chapter 6

Catalytic Asymmetric Hydrosilylation of Ketones. II. Chiral Phosphine-Rhodium Complex-catalyzed Hydrosilylation[1]

SUMMARY

A cationic rhodium complex with (*R*)-benzylmethylphenylphosphine as ligand was found to be effective for asymmetric hydrosilylation of a variety of prochiral ketones. The optical yield markedly depends on the structure of hydrosilanes as well as that of ketones employed. Optical yields up to 61.8% have been achieved. A mechanism involving the formation of diastereomeric α-siloxyalkyl-rhodium intermediates is proposed for the asymmetric hydrosilylation of ketones.

The asymmetric hydrosilylation was also found to be catalyzed by ((-)-DIOP)Rh(S)Cl, where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

INTRODUCTION

Asymmetric reduction of prochiral carbonyl compounds continues to be of interest from both practical and theoretical points of view. Enormous reports[2] of studies have appeared on the asymmetric Meerwein-Ponndorf-Verley reduction, asymmetric Grignard reduction, and reductions by chiral metal hydride complexes. Izumi and coworkers have extensively studied[3] heterogeneous asymmetric hydrogenation of carbonyl compounds, especially acetoacetic acid esters, with a modified Raney nickel catalyst. When we undertook an investigation for the first time

on the catalytic asymmetric hydrosilylation of [illegible] using chiral transition metal complexes as catalysts, definite evidence for an activation of ketone carbonyl by transition metal complexes, had been little known except for the rather special case of hexafluoroacetone.[4]

In Capter 5 we have described[5] that the catalytic hydrosilylation of ketones with methyldichlorosilane proceeds under mild conditions by the use of dichlorobis(dimethylphenylphosphine)-di-μ-chlorodiplatinum(II), and that its chiral phosphine analogs do catalyze the asymmetric hydrosilylation of a series of alkyl phenyl ketones to give, after hydrolysis, partially active 1-phenylalkanols. Although the optical yields obtained there were considerably low, we are convinced that with a proper choice of catalysis higher ability of an asymmetry-inducing catalyst may be disclosed.

In 1970, Schrock and Osborn have reported[6] that a cationic rhodium complex of the type $[RhL_2H_2S_2]^+$, where L is a relatively basic phosphine and S is a solvent, catalyzes the hydrogenation of not only olefinic compounds but also simple ketones under mild conditions. The findings that the cationic complex does activate ketone carbonyls under conditions of hydrogenation greatly influenced our choice of complex. Accordingly, we have prepared a cationic rhodium complex with (*R*)-benzylmethylphenylphosphine (BMPP) as ligand, and catalytic asymmetric hydrosilylation of prochiral ketones has been carried out in the presence of the chiral cationic rhodium complex, the reaction proceeding with much higher enantioselectivity than in the platinum(II) system. In this chapter, we describe in detail the catalytic asymmetric hydrosilylation of ketones, focusing our attention on a dependence of optical yields on the structure of hydrosilane used. After this investigation had been completed, a similar rhodium complex-catalyzed asymmetric hydrosilylation of ketones was reported independently by three research groups.[7,8,9]

RESULTS AND DISCUSSION

Cationic rhodium complex, $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (1) (NBD = 2,5-norbornadiene), was prepared according to the procedure reported by Schrock and Osborn,[10] from the reaction of di-μ-chlorobis(2,5-norbornadiene)dirhodium with (*R*)-benzylmethylphenylphosphine in the presence of sodium perchlorate. 1 was then treated with molecular hydrogen in benzene-dichloromethane (5:1) solution to give *in situ* $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (2) (S = solvent), which was used as a catalyst precursor for the present hydrosilylation (eq. 1 and 2).

$$\frac{1}{2}[Rh(NBD)Cl]_2 + 2L^* \xrightarrow{NaClO_4} [RhL^*_2(NBD)]^+ClO_4^- \quad (1)$$

1

$[\alpha]_D^{20}$ +29° (*c* 0.3, CH_2Cl_2)

$$[RhL^*_2(NBD)]^+ClO_4^- \xrightarrow[C_6H_6/CH_2Cl_2]{H_2} [RhL^*_2H_2S_2]^+ClO_4^- \quad (2)$$

1 2

L* = (*R*)-$(PhCH_2)MePhP$ (70 or 79% optical purity)

Attempts to prepare cationic rhodium complex $[Rh\{(-)\text{-DIOP}\}(NBD)]^+ClO_4^-$, where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane,[11] were unsuccessful, and known $((-)\text{-DIOP})Rh(S)Cl$[11] was used. Recently, Kagan and coworkers have reported[8] that $((+)\text{-DIOP})Rh(S)Cl$ is an effective catalyst for asymmetric hydrosilylation of ketones.

Asymmetric hydrosilylation of ketones catalyzed by $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (2)

All experiments were carried out in degassed sealed glass tubes. In typical runs the catalyst concentration was 5×10^{-4} mole per mole of a ketone and an equivalent of a hydrosilane for the ketone was used. The mixture was heated at a given temperature for 40 hr. The hydrosilylation proceeded almost quantitatively. The hydrosilylation product, a silyl ether of a *sec*-alcohol, was isolated by distillation and characterized by ir and nmr spectra and elemental analyses. The silyl ether was then converted into the corresponding *sec*-alcohol by treatment with potassium hydroxide in aqueous methanol or with excess methyllithium followed by acid hydrolysis (eq. 3). Absolute configuration

$$R^1COR^2 + HSiR_3 \xrightarrow{\underset{\sim}{2}} R^1R^2\overset{*}{C}HOSiR_3 \longrightarrow R^1R^2CHOH \qquad (3)$$

and optical purity of the *sec*-alcohol thus obtained were determined on the basis of the known maximum rotation of the pure enantiomer. All results obtained are summarized in Tables I, II, and III.

In the first set of experiments (Table I), the asymmetric addition of trialkylsilanes to a series of alkyl phenyl ketones in the presence of $\underset{\sim}{2}$ was found to give predominantly (*S*)-1-phenylalkanols with one exception. Fairly good optical yields were obtained from the reaction of alkyl phenyl ketones, except for 2-phenylacetophenone, with phenyldimethylsilane. The optical yields of 31.6, 43.1, 56.3, and 61.8% for acetophenone, propiophenone, isobutyrophenone, and pivalophenone, respectively, are much higher than those observed in asymmetric hydrosilylation of the corresponding ketones catalyzed by platinum(II)[5] with the same chiral phosphine as used here. These values may well be compared with those reported in stoichiometric reductions of ketones using chiral Grignard reagents or chiral metal hydride

Table I. Asymmetric Hydrosilylation of Alkyl Phenyl Ketones with $HSiR_3$ Catalyzed by $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ [a] at 50° for 40 hr.

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol[b] $[\alpha]_D^{20}$ (neat)	Optical yield[c] (%) (Configuration)
$HSiR_3 = HSiMe_2Ph$				
MeCOPh	97	-19.21	-9.61	31.6 (*S*)
EtCOPh	94	-24.54	-8.47	43.1 (*S*)
i-PrCOPh	62	-28.48	-18.81[d]	56.3 (*S*)
t-BuCOPh	84	-24.92	-11.20[e]	61.8 (*S*)
$PhCH_2COPh$	44	-0.30	0[f]	—
$HSiR_3 = HSiMe_3$				
MeCOPh	100	-2.25	-1.55	5.1 (*S*)
EtCOPh	92	-3.23	-1.26	6.4 (*S*)
i-PrCOPh	98	-1.78	-1.23[d]	3.7 (*S*)
t-BuCOPh	81	+10.50	+5.10[e]	28.1 (*R*)
$PhCH_2COPh$	70	-0.37	0[f]	—
$HSiR_3 = HSiMePh_2$				
EtCOPh	65[g]	-9.67	-4.00	20.3 (*S*)
$HSiR_3 = HSiMeEt_2$				
EtCOPh	42[h,i]	-0.55	-0.28	1.3 (*S*)

[a] The phosphine of 70% optical purity was used unless otherwise noted. [b] The specific rotations of pure enantiomers reported are: (*S*)-1-phenylethanol; $[\alpha]_D^{24}$ -43.5° (neat),[16] (*S*)-1-phenylpropanol; $[\alpha]_D^{22}$ -28.1° (neat),[16] (*S*)-2-methyl-1-phenylpropanol; $[\alpha]_D^{20}$ -47.7° (ether),[16] (*R*)-2,2-dimethyl-1-phenylpropanol; $[\alpha]_D^{22}$ +25.9° (benzene),[16] (*S*)-1,2-diphenylethanol; $[\alpha]_D^{20}$ +56.1° (ethanol).[17] The enantiomeric purities of these 1-phenylalkanols

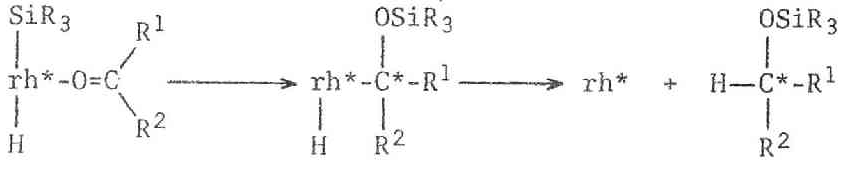
Table I. (continued)

were also determined directly by nmr measurement with the aid of a chiral shift reagent, tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III).[18] [c] Corrected for the optical purity of the chiral phosphine used. [d] Specific rotation in ether. [e] In benzene. [f] In ethanol. [g] Heated at 80° for 120 hr. [h] Heated at 70° for 50 hr. [i] The phosphine of 79% optical purity was used.

complexes such as $LiAlH_m(OR^*)_n$.[1,12]

It should be noted that the extent of asymmetric hydrosilylation depends strongly upon the structure of hydrosilanes employed: with phenyldimethylsilane optical yields are generally more than several times as high as with trimethylsilane. Most remarkable is the fact that the addition of phenyldimethylsilane to pivalophenone gave the silyl ether of (*S*)-2,2-dimethyl-1-phenylpropanol, while trimethylsilane led to the *R* enantiomer. The marked effect of silane structure on a stereochemical outcome may be best rationalized as proceeding in the sequence depicted by Scheme I.

Scheme I



A

The proposed mechanism involves the following steps. (a) Oxidative addition of the hydrosilane to the cationic rhodium complex which is coordinated with ketones like solvent. (b) The resulting silicon-rhodium moiety undergoes insertion of the ketone carbonyl, which is activated by its coordination with the

rhodium complex, to form diastereomeric α-siloxyalkyl-rhodium intermediates A. Finally, (c) the product, an optically active silyl ether of a *sec*-alcohol, is certainly formed from reductive elimination of the diastereomeric intermediates. Of these steps, step (b) must play the most important role in inducing asymmetry at the carbonyl carbon because of the formation of a pair of diastereomeric α-siloxyalkyl-rhodium intermediates, in which a predominant configuration and the extent of enantiomeric excess of the product would have already been determined. It is, therefore, reasonable that the steric demands of not only the chiral phosphine ligand but also the substituents on the silicon bound to the rhodium catalyst exhibit a remarkable effect on the selection of enantiotopic faces of a prochiral ketone.

Such marked effects of the structure of hydrosilanes as mentioned above on the stereoselectivity have not been observed in the asymmetric hydrosilylation of prochiral olefins.[13] Since the key step in the hydrosilylation of olefins is the formation of alkylmetal intermediates which arise from the insertion of a coordinated olefin to a hydridometal moiety, the silyl group, which is still bound to the metal throughout the course of formation of the alkylmetal intermediates, may not exert any significant steric effect on the stereoselectivity.

It is conceivably possible to argue that the hydrosilylation of ketones proceeds, by analogy to that of olefins, *via* alkoxyrhodium intermediates which arise from the insertion of ketone carbonyl into the hydridorhodium moiety. In fact, the intervention of an alkoxyrhodium has been proposed by Schrock and Osborn for the hydrogenation of ketones catalyzed by cationic rhodium complexes.[6] However, such a mechanism involving alkoxyrhodium intermediates would not give rise to the observed changes in optical yields on changing the silane structure. In addition, the fact that the asymmetric hydrogenation of acetophenone catalyzed by the same chiral rhodium complex 2 has been found to

Table II. Asymmetric Hydrosilylation of Dialkyl Ketones with $HSiR_3$ Catalyzed by $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ at 50° for 40 hr.

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol[a] $[\alpha]_D^{20}$ (neat)	Optical yield[b] (%) (Configuration)
$HSiR_3 = HSiMe_2Ph$				
$PhCH_2COMe$	69	+3.74	+3.02	15.3 (*S*)
t-BuCOMe	46	0	-0.10	1.8 (*R*)
n-BuCOMe	64	-0.23	-0.44	5.4 (*R*)
$HSiR_3 = HSiMe_3$				
$PhCH_2COMe$	76	+3.68	+1.96	10.0 (*S*)
t-BuCOMe	75	-0.15	-0.09	1.6 (*R*)
n-BuCOMe	82	-0.32	-0.36	4.4 (*R*)
EtCOMe	79	+0.03	0	—

[a] The specific rotations of pure enantiomers are: (*R*)-1-phenylpropan-2-ol; $[\alpha]_D^{25}$ -28.1° (neat),[19] (*S*)-3,3-dimethylbutan-2-ol; $[\alpha]_D^{20}$ +7.84° (neat),[20] (*S*)-hexan-2-ol; $[\alpha]_D^{18}$ +11.68° (neat),[21] (*S*)-butan-2-ol; $[\alpha]_D^{20}$ +13.83° (neat).[19] [b] Corrected for the optical purity of the phosphine used (70%).

give (*R*)-1-phenylethanol in a low optical yield[14] may reinforce the argument on the difference in the key steps between hydrogenation and hydrosilylation of ketones.

Ojima and coworkers have previously reported[15] steric effects of hydrosilanes similar to those mentioned above in the stereoselective hydrosilylation of terpene ketones such as menthone or camphor.

Hydrosilylation of several dialkyl ketones with phenyldimethylsilane and trimethylsilane in the presence of 2 was also

carried out (Table II). The results show that no significant asymmetric induction was observed in the hydrosilylation of 3,3-dimethyl-2-butanone, 2-hexanone, and 2-butanone. On the other hand, the reaction of 1-phenyl-2-propanone with either hydrosilane gave the respective silyl ethers of (*S*)-1-phenyl-2-propanol in higher than 10% optical yield. Therefore, it may be said that the presence of a phenyl group in the ketone substrate, such as 1-phenyl-2-propanone and alkyl phenyl ketones, necessarily favors the asymmetric induction in the present reaction systems.

The addition of dialkylsilanes to ketones in the presence of 2 proceeded readily at 20° to give optically active silyl ethers, the results obtained being shown in Table III. Several features may be drawn from Table III. With dialkylsilanes occasional formation of silyl enol ethers accompanying the asymmetric addition reaction was observed (see footnote *b* in Table III). Of interest is that with any of the dialkylsilanes propiophenone always gave a silyl ether of (*R*)-1-phenylpropanol in contrast to the reaction with trialkylsilanes. Furthermore, it is noteworthy that an optical yield in the hydrosilylation of 3,3-dimethyl-2-butanone was much improved by the use of dialkylsilanes, while the reaction with trialkylsilanes gave no appreciable asymmetric induction.

In conclusion, all results described here clearly indicate that an exquisite match of ketone and hydrosilane with a given chiral catalyst does attain a high optical yield, though the choice of the catalyst is only empirical at the present time.

Asymmetric hydrosilylation of ketones catalyzed by ((-)-DIOP)-Rh(S)Cl (3)

The ability of 3 as an catalyst for the asymmetric hydrosilylation of ketones was also examined. The addition of dialkylsilanes to alkyl phenyl ketones in the presence of 3 took

Table III. Asymmetric Hydrosilylation of Ketones with H_2SiR_2 Catalyzed by $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (2) at 20° for 40 hr.

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol $[\alpha]_D^{20}$ (neat)	Optical yield[a] (%) (Configuration)
$H_2SiR_2 = H_2SiEt_2$				
EtCOPh	91[b]	+0.87	+0.45	2.0 (*R*)
t-BuCOPh	78	+1.06[c]	+0.59[d]	3.3 (*R*)
t-BuCOMe	90	-3.23	-1.42	23.0 (*R*)
$H_2SiR_2 = H_2SiPh_2$				
MeCOPh	84	+7.83	+6.34	14.6 (*R*)
EtCOPh	83	+2.11	+0.96	4.4 (*R*)
t-BuCOMe	84	-2.16	-1.39	22.5 (*R*)
$H_2SiR_2 = H_2SiMePh$				
EtCOPh	84[e]	—	+2.59	11.7 (*R*)

[a] Optical yield is calculated on the basis of specific rotation of pure enantiomer (see the footnotes in Tables I and II), and corrected for the optical purity of the phosphine used (79%). [b] Including 17% of $Ph(HSiEt_2O)C{=}CHCH_3$. [c] The chiral phosphine of 70% optical purity was used. [d] In benzene. [e] A mixture of diastereoisomers associated with asymmetric silicon atom (*ca.* 1:1 by nmr analysis).

place well at 50° to give (*R*)-adduct predominantly except for the silyl ether of (*S*)-2,2-dimethyl-1-phenylpropanol from the reaction between pivalophenone and diphenylsilane. Hydrosilylation of alkyl phenyl ketones with trialkylsilanes, on the other hand, required higher reaction temperature, and the optical yields were

Table IV. Asymmetric Hydrosilylation of Alkyl Phenyl Ketones Catalyzed by ((-)-DIOP)Rh(S)Cl[a] (3) at 50° for 40 hr.

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol $[\alpha]_D^{20}$ (neat)	Optical yield (%) (Configuration)
Silane = H_2SiEt_2				
MeCOPh	90	+14.13	+11.59	26.6 (*R*)
EtCOPh	83	+26.97	+12.89	45.9 (*R*)
i-PrCOPh	89	+5.37	+4.69[b]	9.8 (*R*)
t-BuCOPh	83	-12.02	-6.56[c]	25.3 (*S*)
Silane = H_2SiPh_2				
MeCOPh	81	+16.43	+13.29	30.6 (*R*)
EtCOPh	81	+17.40	+7.92	28.2 (*R*)
i-PrCOPh	72	+16.63	+13.07[b]	27.4 (*R*)
t-BuCOPh	75	+20.47	+10.63[c]	41.0 (*R*)
Silane = $HSiMe_2Ph$				
MeCOPh[d]	35	+2.46	—	2.8[e] (*R*)
EtCOPh[d]	54	+3.94	—	4.8[e] (*R*)
t-BuCOPh[d]	41	+9.51	—	16.5[e] (*R*)
Silane = $HSiMe_3$				
EtCOPh[d]	62	+3.21	—	4.4[e] (*R*)
t-BuCOPh[f]	83	+7.57	—	14.2[e] (*R*)

[a] Catalyst = 0.1 mol%. [b] Specific rotation in ether. [c] In benzene. [d] Heated at 70°. [e] Optical yield was calculated on the basis of specific rotation of the optically pure silyl ethers which was estimated by data indicated in Table I. [f] Heated at 90°.

generally much lower than with dialkylsilanes. The data obtained for asymmetric hydrosilylation catalyzed by 3 were summarized in Table IV. The marked dependence of the optical yields on the structure of hydrosilanes was also observed in this catalyst system.

Very recently, Kagan and coworkers have reported[8] similar results by the use of ((+)-DIOP)Rh(S)Cl or a polymer-supported rhodium complex related to it. α-Naphthylphenylsilane is found to be most useful.

EXPERIMENTAL

General comments

A Varian Aerograph Model 90P, equipped with a 20 ft. column packed with Silicone DC550 (30% on Celite) or PEG 20M (30% on Celite), was used for isolation and purification of the products. Nmr spectra were obtained on a Varian EM-360 spectrometer, ir spectra with a Hitachi EPI-G3 Grating spectrophotometer, and optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter.

(*R*)-benzylmethylphenylphosphine (BMPP)[22] and (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)[11] were prepared by the reported methods.

Preparation of $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (1)

The procedure reported by Schrock and Osborn[10] for preparing the complexes of the type $[RhP_2(NBD)]^+ClO_4^-$ (P = tertiary phosphine) was modified as follows: Under an argon atmosphere 0.40 g (0.87 mmol) of di-μ-chlorobis(2,5-norbornadiene)dirhodium and 0.25 g (2.02 mmol) of sodium perchlorate were placed in a 30 ml flask, and 1.7 ml of degassed tetrahydrofuran was added. To the suspension, 0.77 g (3.62 mmol) of (*R*)-BMPP (79% optical purity)

was added dropwise with stirring. The mixture was stirred for 10 min, and then 15 ml of anhydrous ether was added dropwise to the red cloudy solution. The orange precipitates formed were filtered, and the filtered cake was then dissolved with dichloromethane, leaving sodium chloride behind. The dichloromethane solution was reduced to 1 ml *in vacuo* and 12 ml of anhydrous ether was added. The orange powder was filtered off, washed two portions of each 5 ml of ether, and dried *in vacuo* to give 1.20 g (95%) of 1: $[\alpha]_D^{20}$ +29° (*c* 0.275, dichloromethane). *Anal* Calcd for $C_{35}H_{38}O_4ClP_2Rh$: C, 58.15; H, 5.30; Cl, 4.90. Found: C, 56.54; H, 5.83; Cl, 5.19. The same complex but with the phosphine of 70% optical purity was also prepared.

1 was treated with molecular hydrogen in benzene/dichloromethane (5:1) solution to generate $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (2) with the elimination of norbornane. The solvated dihydrido species was used as a catalyst for the present reaction.

Asymmetric hydrosilylation of ketones

All reactions were carried out in glass ampoules. A ketone (40 mmol), a hydrosilane (40 mmol), and a chiral catalyst (2 or 4×10^{-2} mmol) were placed in a glass ampoule, and the mixture was degassed by several freeze-thawings under reduced pressure. The ampoule was then sealed *in vacuo* and heated over a period of 40 hr. The product was isolated by fractional distillation or by preparative glc after flash distillation to give an optically active silyl ether. The silyl ether was characterized by ir and nmr spectra and elemental analyses. These data were listed in Tables V and VI. The silyl ether was converted into the corresponding alcohol by hydrolysis with potassium hydroxide in aqueous methanol where possible, or by methylation with excess methyllithium followed by acid hydrolysis. The optical yield was determined by comparison of specific rotation of the obtained alcohol with that of the pure enantiomer which was reported in

Table V. Physical Constants and Analytical Data for Hydrosilylation Products.

Compound	bp (°C/mm)	n_D^{20}	d_4^{20}	C% Found(Calcd.)	H% Found(Calcd.)
$MePhCHOSiMe_2Ph$	118/3	1.5314	0.9955	74.90(74.95)	7.81(7.86)
$EtPhCHOSiMe_2Ph$	123/3	1.5272	0.9863	75.74(75.50)	8.41(8.20)
i-$PrPhCHOSiMe_2Ph$	124/2.5	1.5233	0.9771	76.10(76.00)	8.57(8.50)
t-$BuPhCHOSiMe_2Ph$	118/2.5	1.5218	0.9726	76.20(76.45)	8.99(8.78)
$PhCH_2PhCHOSiMe_2Ph$	145-49/0.02	1.5622	1.0372	79.26(79.47)	7.13(7.28)
$PhCH_2MeCHOSiMe_2Ph$	137/5	1.5267	0.9850	75.80(75.50)	8.40(8.20)
t-$BuMeCHOSiMe_2Ph$	96/3	1.4783	0.9051	71.36(71.12)	10.42(10.23)
n-$BuMeCHOSiMe_2Ph$	97/4	1.4761	0.9018	71.24(71.12)	10.52(10.23)
$MePhCHOSiMe_3$[a]	49.5/3	1.4704	0.9026	68.27(67.98)	9.60(9.33)
$EtPhCHOSiMe_3$	62/3.5	1.4697	0.8974	69.13(69.17)	9.87(9.67)
i-$PrPhCHOSiMe_3$	61/2.5	1.4697	0.8929	70.13(70.21)	10.21(9.97)
t-$BuPhCHOSiMe_3$	63/3	1.4711	0.8971	71.36(71.12)	10.27(10.23)
$PhCH_2PhCHOSiMe_3$	120.5/3.5	1.5230	0.9766	75.52(75.50)	8.41(8.20)
$PhCH_2MeCHOSiMe_3$[b]	59/5	1.4691	—	—	—
t-$BuMeCHOSiMe_3$	58/41	1.4030	0.7861	62.29(62.00)	12.71(12.72)
n-$BuMeCHOSiMe_3$[c]	70/44	1.4026	—	—	—
$EtMeCHOSiMe_3$[d]	58/110	1.3895	—	—	—

Table V. (continued)

$EtPhCHOSiMePh_2$	150/0.03	1.5684	1.0422	79.60(79.47)	7.23(7.28)
$EtPhCHOSiMeEt_2$	84/3	1.4778	0.9062	71.24(71.12)	10.25(10.23)
$MePhCHOSiHEt_2$	41/2	1.4820	0.9147	69.18(69.17)	9.56(9.68)
$EtPhCHOSiHEt_2$	55/3	1.4872	0.9114	70.04(70.21)	10.04(9.97)
i-$PrPhCHOSiHEt_2$	86.5/3	1.4967	0.9062	71.37(71.12)	10.25(10.23)
t-$BuPhCHOSiHEt_2$	87/3	1.4796	0.9029	71.63(71.93)	10.58(10.46)
t-$BuMeCHOSiHEt_2$	100-2/70	1.4189	0.8086	63.54(63.76)	12.62(12.84)
$MePhCHOSiHPh_2$	139/0.03	1.5802	1.0625	78.61(78.90)	6.46(6.62)
$EtPhCHOSiHPh_2$	145/0.09	1.5741	1.0521	79.39(79.20)	7.15(6.96)
i-$PrPhCHOSiHPh_2$	165/0.2	1.5671	1.0394	79.32(79.47)	7.32(7.26)
t-$BuPhCHOSiHPh_2$	170-3/0.03	1.5655	1.0326	79.86(79.72)	7.47(7.56)
t-$BuMeCHOSiHPh_2$	124/3	1.5303	0.9798	76.24(76.00)	8.68(8.50)
$EtPhCHOSiHMePh$	115-25/3	—	—	74.68(74.95)	7.95(7.86)

[a] lit.[23], bp 91° (14 mm), n_D^{20} 1.4702, d_4^{20} 0.9059. [b] lit.[23], bp 102° (18 mm), n_D^{20} 1.4690, d_4^{20} 0.8974. [c] lit.[24] bp 154-155° (741 mm), n_D^{20} 1.4020, d_4^{20} 0.7856. [d] lit.[25], bp 112.3°, n_D^{20} 1.3898, d_4^{20} 0.772.

Table VI. ^{1}H nmr Data for Hydrosilylation Products.

a) $R^1R^2CHOSiMe_2Ph$

R^1	R^2	$Si(CH_3)_2$[a]	OCH	SiC_6H_5	Others
Me	Ph	0.24 0.31	4.75(q, J = 6.0 Hz)	7.03-7.55(m)	1.38(d, J = 6.0 Hz, CCH_3) 7.16(s, C_6H_5)
Et	Ph	0.19 0.25	4.45(t, J = 6.6 Hz)	7.04-7.54(m)	0.79(t, J = 6.6 Hz, CH_2CH_3) 1.66(5, ill resolved, CH_2CH_3) 7.15(s, C_6H_5)
i-Pr	Ph	0.17 0.21	4.23(d, J = 6.2 Hz)	6.90-7.50(m)	0.73 and 0.90(a pair of d, J = 6.2 Hz, $C(CH_3)_2$) 1.79(7, J = 6.2 Hz, CH) 7.12(s, C_6H_5)
t-Bu	Ph	0.17	4.19(s)	6.85-7.64(m)	0.86(s, $C(CH_3)_3$) 7.14(s, C_6H_5)
$PhCH_2$	Ph	0.03 0.09	4.73(t, J = 6.4 Hz)	6.9-7.4(m)	2.88(d, J = 6.4 Hz, CH_2) 7.23(s, $2C_6H_5$)
$PhCH_2$	Me	0.15 0.19	3.93(6, J = 6.4 Hz)	7.36(broad s)	1.10(d, J = 6.4 Hz, CCH_3) 2.66(d, J = 6.4 Hz, CH_2) 7.17(s, C_6H_5)

Table VI. (continued)

t-Bu	Me	0.37	3.49(q, J = 6.2 Hz)	7.24-7.72(m)	0.87(s, $C(CH_3)_3$) 1.01(d, J = 6.2 Hz, CH_3)
n-Bu	Me	0.31	3.74(6)	7.19-7.72(m)	0.6-1.5(broad m, *n*-butyl) 1.02(d, J = 6.6 Hz, $OCCH_3$)

b) $R^1R^2CHOSiMe_3$

R^1	R^2	$Si(CH_3)_3$	OCH	Others
Me	Ph	0.03(s)	4.77(q, J = 6.0 Hz)	1.37(d, J = 6.0 Hz, CCH_3), 7.22(s, C_6H_5)
Et	Ph	0.12(s)	4.60(t, J = 6.4 Hz)	0.96(t, J = 7.2 Hz, CH_2CH_3), 1.75(5, ill resolved, CH_2CH_3), 7.32(s, C_6H_5)
i-Pr	Ph	0.09(s)	4.36(d, J = 6.2 Hz)	0.87 and 0.99(a pair of d, J = 6.2 Hz, $C(CH_3)_2$), 1.59-2.20(m, CH), 7.31(s, C_6H_5)
t-Bu	Ph	0.02(s)	4.31(s)	0.92(s, $C(CH_3)_3$), 7.92(s, C_6H_5)
$PhCH_2$	Ph	-0.09(s)	4.78(t, J = 6.2 Hz)	2.94(d, J = 6.2 Hz, CH_2), 7.23(s, $CH_2C_6H_5$), 7.31(s, OCC_6H_5)
$PhCH_2$	Me	-0.12(s)	3.91(6, J = 6.2 Hz)	1.11(d, J = 6.2 Hz, CH_3), 2.64(d, J = 6.4 Hz, CH_2), 7.25(s, C_6H_5)
t-Bu	Me	0.14(s)	3.44(q, J = 6.4 Hz)	0.89(s, $C(CH_3)_3$), 1.08(d, J = 6.4 Hz, $OCCH_3$)
n-Bu	Me	0.08(s)	3.62(6, ill resolved)	0.6-1.5(broad m, *n*-butyl), 1.09(d, J = 6.4 Hz, $OCCH_3$)

Table VI. (continued)

c) $R^1R^2CHOSiHEt_2$[b]

R^1	R^2	Si*H*[c]	OC*H*	Others[d]
Me	Ph	4.32(5)	4.57(q, J = 6.4 Hz)	1.42(d, J = 6.4 Hz, CH_3), 7.26(s, C_6H_5)
Et	Ph	4.41(5)	4.55(t, J = 6.2 Hz)	0.89(t, J = 6.8 Hz, CH_3), 1.70(5, CH_2) 7.25(s, C_6H_5)
i-Pr	Ph	4.32(5)	4.26(d, J = 6.4 Hz)	0.7-2.0(m, $C(CH_3)_2$), 1.80(7, J = 6.4 Hz, CH), 7.18(s, C_6H_5)
t-Bu	Ph	4.34(5)	4.28(s)	0.83(s, $C(CH_3)_3$), 7.23(s, C_6H_5)
t-Bu	Me	4.36(5)	3.40(q, J = 6.4 Hz)	0.85(s, $C(CH_3)_3$), 1.40(d, J = 6.4 Hz, CH_3)

d) $R^1R^2CHOSiHPh_2$[e]

R^1	R^2	Si*H*	OC*H*	Others[f]
Me	Ph	5.39(s)	4.91(q, J = 6.2 Hz)	1.46(d, J = 6.2 Hz, CH_3), 7.20(s, C_6H_5)
Et	Ph	5.35(s)	4.60(t, J = 6.2 Hz)	0.84(t, J = 7.2 Hz, CH_3), 1.78(5, CH_2) 7.12(s, C_6H_5)
i-Pr	Ph	5.27(s)	4.37(d, J = 6.2 Hz)	0.77 and 0.92(a pair of d, J = 7.2 Hz, $C(CH_3)_2$), 1.92(7, CH), 7.14(s, C_6H_5)
t-Bu	Ph	5.24(s)	4.34(s)	0.97(s, $C(CH_3)_3$), 7.14(s, C_6H_5)

Table VI. (continued)

t-Bu	Me	5.41(s)	3.57(q, J = 6.2 Hz)	0.92(s, $C(CH_3)_3$), 1.10(d, J = 6.2 Hz, CH_3)

e) Others

Compound	
$EtPhCHOSiMePh_2$	0.44(s, $SiCH_3$), 0.81(t, J = 6.8 Hz, CH_2CH_3), 1.74(5, CH_2CH_3), 4.59(t, J = 6.0 Hz, OCH), 7.21(s, CC_6H_5), 7.00-7.66(m, SiC_6H_5)
$EtPhCHOSiMeEt_2$	-0.03(s, $SiCH_3$), 0.20-1.22(m, $SiCH_2CH_3$), 0.86(t, J = 7.0 Hz, CH_2CH_3), 1.67(5, CH_2CH_3), 4.52(t, J = 6.0 Hz, OCH), 7.21(s, C_6H_5)
$EtPhCHOSiHMePh$[g]	0.30 and 0.34(d, J = 2.8 Hz, $SiCH_3$), 0.80 and 0.82(t, J = 6.8 Hz, CH_2CH_3), 1.72(5, CH_2CH_3), 4.52(t, J = 6.0 Hz, OCH), 4.91 and 4.99(q, J = 2.8 Hz, SiH), 7.14 and 7.17(s, CC_6H_5), 6.89-7.56(m, SiC_6H_5)

[a] Diastereotopic methyls (a pair of s). [b] ν(Si-H): 2100-2110 cm^{-1}. [c] J = 2.2 Hz: $HSi-CH_2$. [d] $SiCH_2CH_3$: δ 0.3-1.0 (diffused multiplet). [e] ν(Si-H): 2120-2125 cm^{-1}. [f] SiC_6H_5: δ 7.2-7.6 (m). [g] A mixture of two diastereomeric isomers.

the literature (see footnotes in Tables I and II).

All the results obtained for asymmetric hydrosilylation of ketones are collected in Tables I, II, III, and IV. Two examples of the typical procedure are given below.

1. Reaction of pivalophenone with phenyldimethylsilane catalyzed by 2. Through a solution of 14 mg (2×10^{-2} mmol) of 1 (70% optical purity) in 3.0 ml of degassed benzene/dichloromethane (5:1) molecular hydrogen was bubbled for 10 min, and to the catalyst solution 6.5 g (40 mmol) of povalophenone and 5.5 g (40 mmol) of phenyldimethylsilane were added successively. The mixture was heated at 50° over a period of 40 hr in a sealed degassed glass ampoule. The product was isolated by distillation through a short Vigreux column to give 10.0 g (84%) of 2,2-dimethyl-1-phenylpropyl phenyldimethylsilyl ether, bp 118° (2.5 mm), n_D^{20} 1.5218, d_4^{20} 0.9726, $[\alpha]_D^{20}$ -24.92° (neat). The nmr and analytical data are shown in Tables V and VI. To a tetrahydrofuran solution of the silyl ether, a slightly excess amount of methyllithium in ether solution was added. The mixture was heated at reflux for 3 hr, and then hydrolyzed with dilute hydrochloric acid. After working up in a usual manner, fractional distillation gave quantitatively 2,2-dimethyl-1-phenylpropanol, $[\alpha]_D^{20}$ -11.20° (*c* 4, benzene). Absolute configuration and optical purity were determined on the basis of the known values of $[\alpha]_D^{22}$ +25.9° (benzene) for (*R*)-2,2-dimethyl-1-phenylpropanol.[16] Taking account of an optical purity of the phosphine (70%), the optical yield is 61.8%.

2. Reaction of propiophenone with diphenylsilane catalyzed by 3. In a degassed glass ampoule a mixture of 5.4 g (40 mmol) of propiophenone and 7.4 g (40 mmol) of diphenylsilane was heated at 50° for 40 hr in the presence of 9 mg (2×10^{-2} mmol) of di-μ-chlorobis(1,5-hexadiene)dirhodium and 20 mg (4×10^{-2} mmol) of (-)-DIOP. Distillation gave 10.3 g (81%) of 1-phenylpropyl diphenylsilyl ether, bp 143-5° (0.09 mm), n_D^{20} 1.5741, d_4^{20} 1.0521, $[\alpha]_D^{20}$ +17.04° (neat). To a solution of the silyl ether thus obtained

in 20 ml of methanol was added with stirring 15 ml of 2 *N* KOH at room temperature. The hydrolysis was completed within 10 min. After work-up, distillation gave 1-phenylpropanol in quantitative yield, $[\alpha]_D^{20}$ +7.29° (neat), which was of 28.2% enantiomeric excess of the *R* isomer, on the basis of the known value of $[\alpha]_D^{22}$ -28.1° (neat) for (*S*)-1-phenylpropanol.[16]

In the reaction of propiophenone with diethylsilane catalyzed by 2, the asymmetric addition reaction was accompanied by the formation of 17% of 1-diethylsiloxy-1-phenylpropene. The silyl enol ether was isolated by preparative glc, nmr(CCl_4/TMS): δ 0.3-1.2 (m, $SiCH_2CH_3$), 1.77 (d, J =6.8 Hz, $=CCH_3$), 4.58 (q, J = 2.0 Hz, SiH), 5.25 (q, J = 6.8 Hz, $=CH$), and 7.04-7.49 (m, C_6H_5). *Anal* Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.76; H, 9.39.

REFERENCES

1. A preliminary communication has appeared in J. Organometal. Chem., 54, C45 (1973).
2. J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., (1971).
3. Y. Izumi, Angew. Chem. Int. Ed., 10, 871 (1971).
4. M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, Chem. Commun., 502 (1966).
5. K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 46, C65 (1973).
6. R. R. Schrock and J. A. Osborn, Chem. Commun., 567 (1970).
7. I. Ojima, T. Kogure, and Y. Nagai, Chem. Lett., 541 (1973); I. Ojima and Y. Nagai, Chem. Lett., 223 (1974).
8. W. Dumont, J.-C. Poulin, T.-P. Dang, and H. B. Kagan, J. Amer. Chem. Soc., 95, 8295 (1973).
9. R. J. P. Corriu and J. J. E. Moreau, J. Organometal. Chem.,

64, C51 (1974).

10. R. R. Schrock and J. A. Osborn, J. Amer. Chem. Soc., 94, 2397 (1971).
11. T.-P. Dang and H. B. Kagan, Chem. Commun., 481 (1971); *idem*, J. Amer. Chem. Soc., 94, 6429 (1972).
12. I. Jacquet and J. P. Vigneron, Tetrahedron Lett., 2065 (1974), and the references cited therein.
13. T. Hayashi, K. Yamamoto, and M. Kumada, J. Org. Chem., to be submitted.
14. P. Bonvicini, A. Levi, G. Modena, and G. Scorrano, J. C. S. Chem. Commun., 1188 (1972).
15. I. Ojima, M. Nihonyanagi, and Y. Nagai, Bull. Chem. Soc. Japan, 45, 3506 (1972).
16. R. McLeod, F. J. Welch, and H. S. Mosher, J. Amer. Chem. Soc., 82, 876 (1960).
17. G. Berti, F. Bottari, and B. Macchia, Chim. Ind. (Milan), 45, 1527 (1963), Chem. Abstr., 60, 10512a.
18. K. Yamanoto, T. Hayashi, and M. Kumada, Bull. Chem. Soc. Japan, 47, 1555 (1974).
19. J. Kenyon, H. Phillips, and V. P. Pittman, J. Chem. Soc., 1072 (1935).
20. R. H. Pickard and J. Kenyon, J. Chem. Soc., 105, 1115 (1914).
21. T. D. Stewart and D. Lipkin, J. Amer. Chem. Soc., 61, 3299 (1938).
22. K. Nauman, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 91, 7012 (1969).
23. W. Gerrard and K. D. Kilburn, J. Chem. Soc., 1536 (1956).
24. S. H. Langer, S. Connell, and I. Wender, J. Org. Chem., 23, 50 (1958).
25. J. Fertig, W. Gerrard, and H. Herbst, J. Chem. Soc., 1488 (1957).

Chapter 7

Catalytic Asymmetric Hydrosilylation of Ketones. III. Preparation of Chiral Ferrocenylphosphines as New Chiral Ligands[1]

SUMMARY

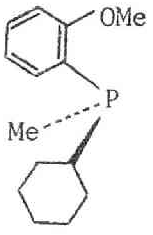
Four chiral ferrocenylphosphines, (*S*)-(*R*)-PPFA, (*R*)-(*S*)-MPFA, (*S*)-(*R*)-BPPFA, and (*R*)-PPEF, all of which contain a planar element of chirality, have been prepared. Their circular dichroism (CD) spectra are recorded.

The chiral phosphines were used as ligands of rhodium complex catalysts in an asymmetric hydrosilylation of ketones. Both (*R*)-(*S*)-MPFA and (*S*)-(*R*)-BPPFA-rhodium complexes were found to catalyze the hydrosilylation of a series of alkyl phenyl ketones and 3,3-dimethyl-2-butanone as efficiently with respect to stereoselectivity as the rhodium complexes with chiral phosphine ligands hitherto described.

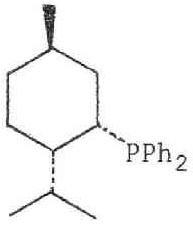
INTRODUCTION

Asymmetric syntheses, especially hydrogenation, catalyzed by transition metal complexes with chiral ligands have recently attracted much interest. One of the crucial problems in studies on the catalytic asymmetric syntheses is how to develop a chiral ligand which will enable the catalyst for a given reaction to be as efficient in stereoselectivity as possible. Although the choice of the chiral ligand for this purpose is only empirical at present, several kinds of chiral phosphines have been prepared and success-

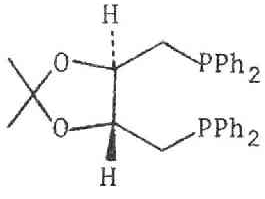
fully used as ligands of the rhodium complex which is one of the most effective catalysts for homogeneous hydrogenation of olefins. These chiral phosphines may be classified into three categories: (a) phosphines bearing an asymmetric center at phosphorus atom,[2] for example, (*R*)-*o*-anisylcyclohexylmethylphosphine (ACMP)[2a] (1), (b) phosphines whose chirality is due to asymmetric carbon atoms in groups bonded to the phosphorus atom, for example, neomenthyldiphenylphosphine (NMDPP)[3] (2), and (c) diphosphines such as (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (DIOP)[4] (3) derived from *L*-threitol.



1



2



3

In this chapter, we describe the preparation of new phosphines with planar chirality which arises from introducing phosphino groups into α-dimethylaminoethylferrocene, and the use of these phosphines as chiral ligands in catalytic asymmetric hydrosilylation of ketones.[5]

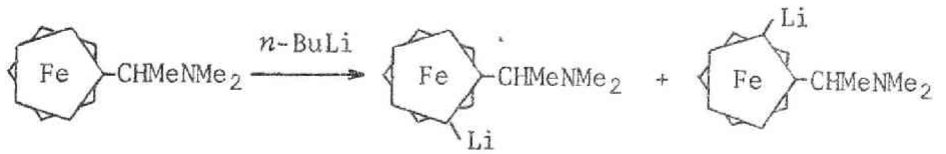
RESULTS AND DISCUSSION

Preparation of chiral ferrocenylphosphines

Chiral ferrocenylphosphines are readily prepared by way of lithiation of resolved α-ferrocenylethyldimethylamine (4). The lithiation of (*R*)-4 has previously been reported by Ugi and coworkers[6] to proceed with high stereoselectivity to give preferentially (*R*)-α-[(*R*)-2-lithioferrocenyl]ethyldimethylamine (5)

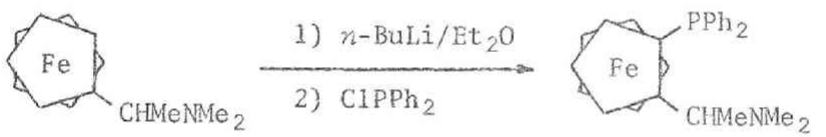
as depicted in Scheme I.

Scheme I.



(*R*)-4 (*R*)-(*R*)-5 (96%) (*R*)-(*S*)-5 (4%)

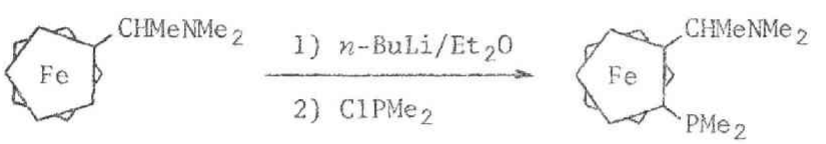
In the present study, (*S*)-4 was metalated with a slight excess of *n*-butyllithium in ether, and the mixture was then treated with chlorodiphenylphosphine to give (*S*)-α-[(*R*)-2-diphenylphosphinoferrocenyl]ethyldimethylamine (PPFA) (eq. 1).



(1)

(*S*)-4 (*S*)-(*R*)-PPFA

In a similar manner, (*R*)-α-[(*S*)-2-dimethylphosphinoferrocenyl]ethyldimethylamine (MPFA) was obtained starting with (*R*)-4 and with chlorodimethylphosphine (eq. 2).

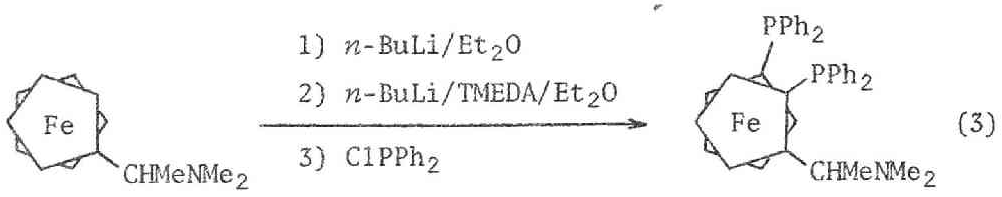


(2)

(*R*)-4 (*R*)-(*S*)-MPFA

The stepwise lithiation of (*S*)-4 with *n*-butyllithium in ether and then with *n*-butyllithium/N,N,N',N'-tetramethylethylenediamine (TMEDA) in ether led to the introduction of two diphenylphosphino

groups into both the cyclopentadienyl rings to give (*S*)-α-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]ethyldimethylamine (BPPFA) (eq.3).

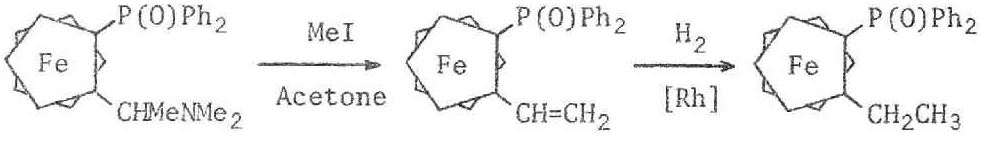


(3)

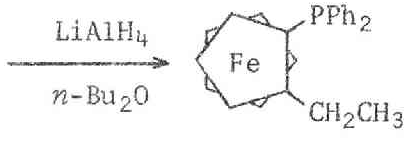
(*S*)-4 (*S*)-(*R*)-BPPFA

Finally, (*R*)-1-diphenylphosphino-2-ethylferrocene (PPEF) having only a planar element of chirality was prepared by a sequence of reactions as depicted in Scheme II. Starting with (*S*)-4, (*S*)-α-[(*R*)-2-diphenylphosphinylferrocenyl]ethyldimethylamine (6) was prepared in a similar way to that for (*S*)-(*R*)-PPFA. 6 was subjected to Hofmann elimination to give (*R*)-1-diphenylphosphinyl-2-vinylferrocene (7). Finally, hydrogenation of 7 to (*R*)-1-diphenylphosphinyl-2-ethylferrocene (8) was followed by reduction with lithium aluminum hydride to give (*R*)-PPEF.

Scheme II



(*S*)-(*R*)-6 (*R*)-7 (*R*)-8



(*R*)-PPEF

Table I. Physical Constants of Chiral Ferrocenylphosphines.

Abbr.	Mp (°C)	$[\alpha]_D^{25}$
(*S*)-(*R*)-PPFA	139	+361° (*c* 0.6, EtOH)
(*R*)-(*S*)-MPFA	oil	-134° (*c* 0.3, $CHCl_3$)
(*S*)-(*R*)-BPPFA	117.5	+345° (*c* 0.5, $CHCl_3$)
(*R*)-PPEF	95.5	+273° (*c* 0.3, $CHCl_3$)

All new compounds were fully characterized by elemental analyses and nmr spectral data. Melting points and specific rotations of these chiral ferrocenylphosphines are summarized in Table I. The absorption and circular dichroism (CD) spectra are shown in Figs. 1 and 2.

The absorption spectrum of ferrocene has two long wavelength bands at 440 and 325 nm assignable to d-d type transition.[7] The CD spectra of chiral ferrocenylphosphines reveal optical activity arising from the planar chirality around these two absorption bands, that is, (*S*)-(*R*)-PPFA, (*S*)-(*R*)-BPPFA, and (*R*)-PPEF all have positive and negative Cotton effects around 450-470 and 340-350 nm respectively, whereas opposite Cotton effects are observed in the case of (*R*)-(*S*)-MPFA.

Asymmetric hydrosilylation of ketones

The asymmetric hydrosilylation of ketones catalyzed by rhodium complexes containing these chiral ferrocenylphosphines as ligands was carried out essentially in the same manner as described in Chapter 6. The asymmetric additions of trialkylsilanes and dialkylsilanes readily took place at 50° and 20°, respectively (eq. 4).

All the results obtained for the asymmetric hydrosilylation catalyzed by (*S*)-(*R*)-PPFA, (*R*)-(*S*)-MPFA, (*S*)-(*R*)-BPPFA, and

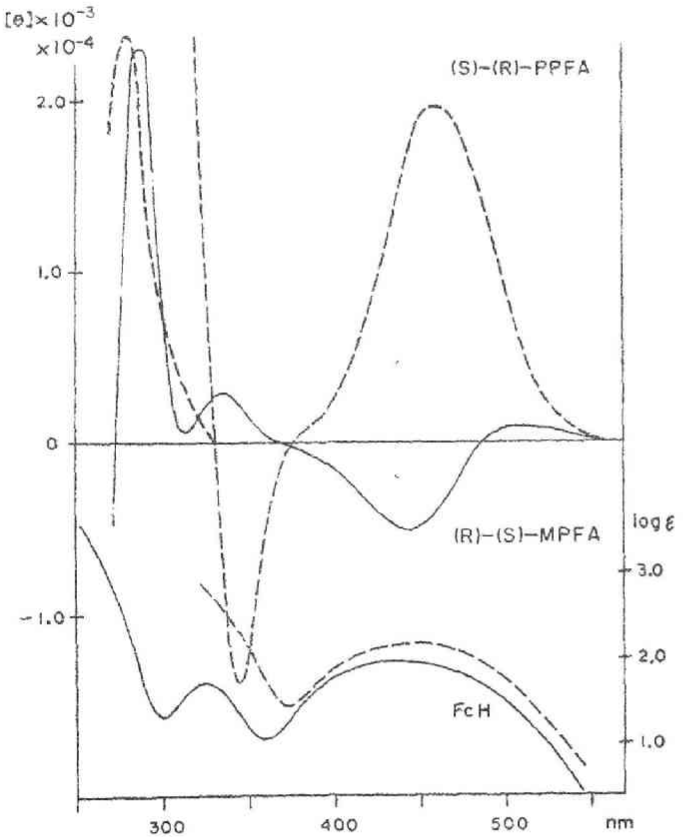


Figure 1. CD and UV spectra of (*S*)-(*R*)-PPFA and (*R*)-(*S*)-MPFA in chloroform.

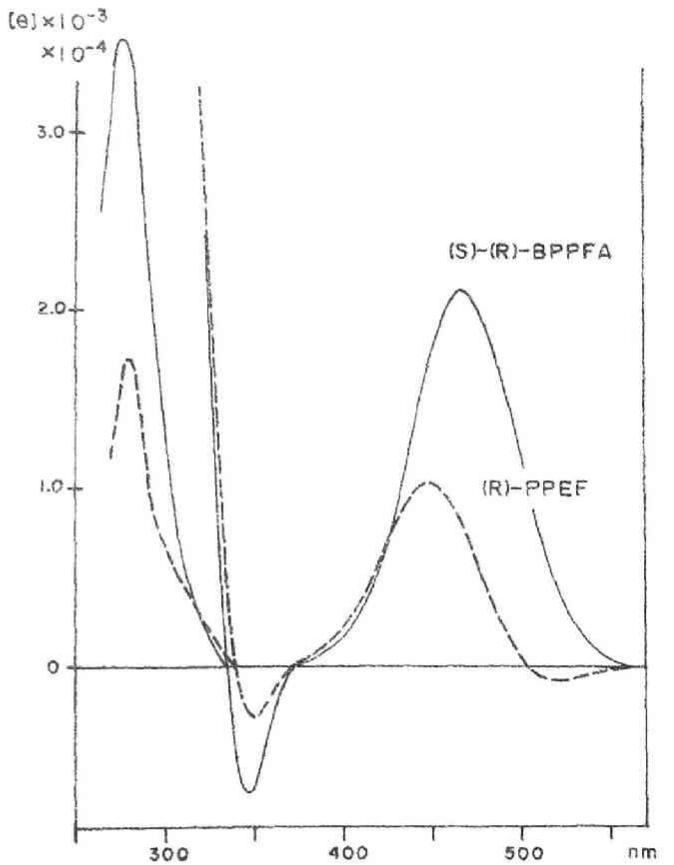


Figure 2. CD spectra of (*S*)-(*R*)-BPPFA and (*R*)-PPEF in chloroform.

Table II. Asymmetric Hydrosilylation of Ketones Catalyzed by (*S*)-(*R*)-PPFA-Rhodium Complex.[a]

Ketone	Silane	Reaction temp (°C)	Yield[b] (%)	Optical purity (%)	Configuration
EtCOPh	$PhMe_2SiH$	50	61	10.5	*R*
EtCOPh	$PhMe_2SiH$[c]	50	40	9.0	*R*
EtCOPh	Me_3SiH	50	84	0.9	*S*
EtCOPh	Et_2SiH_2	20	82	2.7	*R*
EtCOPh	Et_2SiH_2[c]	20	82	2.7	*R*
EtCOPh	Ph_2SiH_2	20	69	0.7	*S*
t-BuCOPh	$PhMe_2SiH$	70	30	10.4	*R*
t-BuCOMe	$PhMe_2SiH$	50	71	19.6	*R*
t-BuCOMe	Ph_2SiH_2	20	88	14.5	*S*

[a] Catalyst = 0.05 mol%. A mixture of di-μ-chlorobis(1,5-hexadiene)dirhodium and two equivalents of (*S*)-(*R*)-PPFA for the rhodium was used unless otherwise noted. [b] Based on the amount of the isolated silyl ether. [c] PPFA/Rh = 1.

(*R*)-PPEF-rhodium complexes are summarized in Tables II, III, IV, and V, respectively.

$$R^1COR^2 + HSiR_3 \xrightarrow{[Rh]^*} R^1R^2\overset{*}{C}HOSiR_3 \qquad (4)$$

$$[Rh]^* : \frac{1}{2}[(C_6H_{10})RhCl]_2 + 2P^*$$

As is seen from these Tables, the extent of asymmetric induction depends strongly upon not only the structure of chiral phosphine ligands but also that of hydrosilanes employed. The marked effect of the latter on the stereoselectivety is very

Table III. Asymmetric Hydrosilylation of Ketones Catalyzed by (*R*)-(*S*)-MPFA-Rhodium Complex.[a]

Ketone	Silane	Reaction temp (°C)	Yield[b] (%)	Optical purity (%)	Configuration
MeCOPh	Ph_2SiH_2	20	85	49.2	*R*
MeCOPh	α-NpPhSiH$_2$	20	74[c]	51.8	*R*
EtCOPh	$PhMe_2SiH$	50	58	12.2	*R*
EtCOPh	Me_3SiH	50	64	7.2	*S*
EtCOPh	Et_2SiH_2	20	88[d]	4.2	*S*
EtCOPh	Ph_2SiH_2	20	83	38.3	*R*
t-BuCOPh	$PhMe_2SiH$	50	75	8.4	*R*
t-BuCOPh	Ph_2SiH_2	20	31	25.3	*S*
t-BuCOMe	$PhMe_2SiH$	50	29	23.5	*S*
t-BuCOMe	Ph_2SiH_2	20	74	41.1	*R*

[a] Catalyst = 0.05 mol%. MPFA/Rh = 2. [b] Based on the amount of the isolated silyl ether. [c] Yield of 1-phenylethanol. [d] Including 20% of $Ph(HSiEt_2O)C{=}CHCH_3$.

characteristic of the asymmetric hydrosilylation of ketones, and has been fully discussed in Chapter 6.

Fairly good optical yields were attained when PPFA, MPFA, or BPPFA was used. For example, the reaction of acetophenone with diphenylsilane catalyzed by (*R*)-(*S*)-MPFA-rhodium complex resulted in higher optical yield than the cases in which (*R*)-benzylmethylphenylphosphine (BMPP)[5a] or DIOP[5a,c] was used as ligands. The high ability of (*R*)-(*S*)-MPFA as an asymmetry inducing ligand was also found in the reaction of 3,3-dimethyl-2-butanone. On the other hand, no significant asymmetric induction was observed when (*R*)-PPEF-rhodium complex was used as a catalyst.

Table IV. Asymmetric Hydrosilylation of Ketones Catalyzed by (*S*)-(*R*)-BPPFA-Rhodium Complex.[a]

Ketone	Silane	Reaction temp (°C)	Yield[b] (%)	Optical purity (%)	Configuration
MeCOPh	Et_2SiH_2	20	92	16.0	*R*
MeCOPh	Ph_2SiH_2	20	72	28.6	*R*
EtCOPh	$PhMe_2SiH$	70	47	8.3	*R*
EtCOPh	Me_3SiH	50	84	1.7	*R*
EtCOPh	Et_2SiH_2	20	84	25.3	*R*
EtCOPh	Ph_2SiH_2	20	73	24.5	*R*
i-PrCOPh	Ph_2SiH_2	20	41	0	—
t-BuCOPh	Et_2SiH_2	20	89	18.3	*S*
t-BuCOPh	Ph_2SiH_2	20	64	3.7	*S*

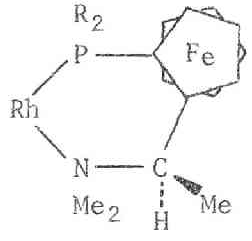
[a] Catalyst = 0.05 mol%. BPPFA/Rh = 1. [b] Based on the amount of the isolated silyl ether.

Table V. Asymmetric Hydrosilylation of Ketones Catalyzed by (*R*)-PPEF-Rhodium Complex.[a]

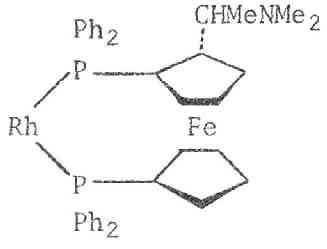
Ketone	Silane	Reaction temp (°C)	Yield[b] (%)	Optical purity (%)	Configuration
EtCOPh	$PhMe_2SiH$	50	46	5.4	*R*
EtCOPh	Me_3SiH	50	88	5.2	*R*
EtCOPh	Et_2SiH_2	20	92	2.2	*R*
EtCOPh	Ph_2SiH_2	20	81	0.2	*S*

[a] Catalyst = 0.05 mol%. PPEF/Rh = 2. [b] Based on the amount of the isolated silyl ether.

PPFA and MPFA are expected to form a chelate with the rhodium atom using both phosphorus and nitrogen atoms[8] (see A), while BPPFA must coordinate to the rhodium with two diphenylphosphino groups present at 1- and 1'-positions of the ferrocene[9] (see B). Despite considerable difference in elements participating



A R = Ph, Me



B

in the chelate formation, it seems likely to presume that these chelate structures with relatively rigid conformations around the rhodium metal[4] would be of advantage in giving rise to a higher asymmetric induction in the present reaction than those with two monodentate PPEF ligands.

It should be mentioned that, in addition to the expected steric effects, attractive interactions between the amino group in the BPPFA ligand and an appropriate prochiral substrate might contribute to the asymmetric potential of the reaction. For example, when BPPFA-rhodium complex is used as a catalyst for asymmetric hydrogenation of an olefinic carboxylic acid, the attractive interactions forming an ammonium carboxylate may be involved. In fact, the hydrogenation of α-acetamidocinnamic acid catalyzed by (*S*)-(*R*)-BPPFA-rhodium complex afforded (*S*)-*N*-acetylphenylalanine with very high stereoselectivity, further studies on the asymmetric hydrogenation being in progress.

EXPERIMENTAL

All melting points described here are uncorrected. ^{1}H nmr spectra were recorded with a Varian EM-360 spectrometer, infrared spectra with a Hitachi EPI-G3 grating spectrophotometer, uv spectra with a Hitachi EPS-3T spectrophotometer, and optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter. ORD and CD spectra were obtained on a JASCO J-20 automatic recording spectropolarimeter.

(*S*)- and (*R*)-α-ferrocenylethyldimethylamine were prepared by the method described in the literature.[6]

Preparation of chiral ferrocenylphosphines

All manipulations for preparing phosphines were carried out in an oxygen-free dry nitrogen atmosphere. Melting points and optical rotations of the phosphines are summarized in Table I.

(*S*)-α-[(*R*)-2-Diphenylphosphinoferrocenyl]ethyldimethylamine (PPFA). According to the procedure reported by Ugi *et al.*[6] for stereoselective lithiation of resolved α-ferrocenylethyldimethylamine (4), 12.4 ml of 1.4 M *n*-butyllithium in *n*-hexane was added to a solution of 3.60 g (14 mmol) of (*S*)-4 ($[\alpha]_D^{24}$ -13.8° (*c* 1.5, ethanol)) in 20 ml of dry ether at 25-27° over a period of 20 min. The mixture was stirred at room temperature for 1.5 hr and then 6.2 g (28 mmol) of chlorodiphenylphosphine in 10 ml of ether was added with heating under gentle reflux during 45 min. After 4 hr reflux aqueous sodium bicarbonate was slowly added with cooling in an ice-bath. The resulting organic layer and benzene extracts from the aqueous layer were combined, washed with water, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to afford a red oil. The oil was chromatographed on alumina (eluent *n*-hexane/benzene, 3/1), and evaporated to give the crude product as orange crystals. The product was purified by recrystallization from ethanol to give 3.11 g (50%) of (*S*)-(*R*)-

PPFA, uv: λ_{max} ($CHCl_3$) 447 nm (ε 150), nmr(CCl_4/TMS): δ 1.19 (d, J = 7.2 Hz, $CHCH_3$), 1.77 (s, NCH_3), 3.90 (s, FeC_5H_5), 3.56-4.39 (m, FeC_5H_3 and $CHCH_3$), and 6.88-7.71 (m, C_6H_5). The ir spectrum indicated the presence of unsubstituted cyclopentadienyl ring (1105 and 1001 cm^{-1}) and phenyl groups (745 and 698 cm^{-1}). ORD (*c* 0.11 and 0.004, chloroform): $[\Phi]_{589}$ +1520°, $[\Phi]_{495}$ +3140° (pk), $[\Phi]_{434}$ +1590° (tr), and $[\Phi]_{294}$ +21,900° (pk). CD spectrum was shown in Figure 1. *Anal* Calcd for $C_{26}H_{28}NPFe$: C, 70.76; H, 6.39; N, 3.17. Found: C, 70.74; H, 6.23; N, 2.95.

(*R*)-α-[(*S*)-2-Dimethylphosphinoferrocenyl]ethyldimethylamine (MPFA). At 27°, 3.14 g (12.2 mmol) of (*R*)-4 ($[\alpha]_D^{24}$ +14.1° (*c* 1.6, ethanol)) was lithiated as described above. To the solution, 1.59 g (15.5 mmol) of chlorodimethylphosphine was added dropwise with stirring. A vigorous reaction occurred and the chlorodimethylphosphine was added at such a rate as to maintain boiling. The resulting mixture was heated under reflux for 3 hr. Benzene/ether (1/1) (50 ml) and dilute sodium hydroxide solution (20 ml) were then added to the cooled reaction mixture. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed on alumina (eluent benzene) to give 1.10 g (31%) of (*R*)-(*S*)-MPFA as a red oil, uv: λ_{max}($CHCl_3$) 446 nm (ε 131), nmr($CDCl_3$): δ 1.08 and 1.31 (a pair of d, J = 2.6 Hz, $P(CH_3)_2$), 1.34 (d, J = 5.6 Hz, $CHCH_3$), 2.14 (s, NCH_3), 4.09 (s, FeC_5H_5), and 3.8-4.4 (m, FeC_5H_3). Methine-proton resonances may lie under the cyclopentadienyl proton resonances. The ir spectrum indicated the presence of unsubstituted cyclopentadienyl ring (1106 and 1000 cm^{-1}) and dimethylphosphino group (928 cm^{-1}). ORD(*c* 0.11 and 0.01, chloroform): $[\Phi]_{589}$ -425°, $[\Phi]_{473}$ -1120° (tr), $[\Phi]_{415}$ -615° (pk), $[\Phi]_{328}$ -1580° (tr), $[\Phi]_{304}$ -990° (pk), and $[\Phi]_{273}$ -8290° (tr). CD spectrum was shown in Figure 1. *Anal* Calcd for $C_{16}H_{24}NPFe$: C, 60.59; H, 7.63; N, 4.42. Found: C, 60.61; H, 7.71; N, 4.51.

(*S*)-α-[(*R*)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl-

dimethylamine (BPPFA). To a solution of 3.6 g (14 mmol) of (*S*)-4 in 22 ml of dry ether, 12.0 ml of 1.4 M *n*-butyllithium in *n*-hexane was added at 27° over a period of 20 min. The mixture was stirred at room temperature for 1 hr and then a mixture of 1.9 g (16 mmol) of freshly distilled TMEDA and 13.0 ml of 1.4 M *n*-butyllithium in *n*-hexane was added in 15 min. After 3.5 hr stirring at room temperature, 9.3 g (42 mmol) of chlorodiphenylphosphine was added to the cooled reaction mixture. After standing overnight it was hydrolyzed with aqueous sodium bicarbonate. The resulting organic layer and extracts (benzene 50 ml) from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed on alumina (eluent *n*-hexane/benzene, 2/1) to give 3.24 g (37%) of the crude (*S*)-(*R*)-BPPFA. A pure sample was obtained as orange crystals by recrystallization from ethanol, uv: $\lambda_{max}(CHCl_3)$ 443 nm (ε 194), nmr (CCl_4/TMS): δ 1.12 (d, J = 7.2 Hz, $CHCH_3$), 1.75 (s, NCH_3), 3.41-4.42 (m, $C_5H_4FeC_5H_3$), and 6.87-7.66 (m, C_6H_5). Methine proton resonances may lie under the cyclopentadienyl proton resonances. The ir spectrum did not exhibit absorptions near 1100 and 1000 cm^{-1}, indicating the absence of unsubstituted cyclopentadienyl rings. ORD(*c* 0.10 and 0.004, chloroform): $[\Phi]_{589}$ +2160°, $[\Phi]_{499}$ +3890° (pk), $[\Phi]_{446}$ +2680° (tr), and $[\Phi]_{299}$ +30,300° (pk). CD spectrum was shown in Figure 2. *Anal* Calcd for $C_{38}H_{37}NP_2Fe$: C, 72.97; H, 5.96; N, 2.24. Found: C, 72.72; H, 6.00; N, 2.49.

(*S*)-α-[(*R*)-2-Diphenylphosphinylferrocenyl]ethyldimethylamine (6). A solution of 8.8 g (37 mmol) of diphenylphosphinic chloride in 30 ml of ether was added in 15 min to the refluxing solution of 5.08 g (19.8 mmol) of (*S*)-4 which had been lithiated as described in the preparation of PPFA. The mixture was refluxed for 9 hr, and then hydrolyzed with aqueous sodium hydroxide. The resulting organic layer and benzene extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to a minimum volume. The residue was

chromatographed on alumina. Elution with benzene gave 2.5 g of starting amine (*S*)-4. Elution with benzene/ethyl acetate (1/1) gave the crude product. The product was purified by recrystallization from dichloromethane/light petr.-ether (1/4) to give 2.74 g (30%) of (*S*)-(*R*)-6 which gave brown crystals, mp 239-242° (decomp.), $[\alpha]_D^{25}$ +161° (*c* 0.40 chloroform), uv: $\lambda_{max}(CHCl_3)$ 446 nm (ε 145), nmr(CCl_4/TMS): δ 1.12 (d, *J* = 6.0 Hz, $CHCH_3$), 1.61 (s, NCH_3), 4.13 (s, FeC_5H_5), 3.76-4.51 (m, FeC_5H_3), and 7.13-8.02 (m, C_6H_5). Methine proton resonances may lie under the cyclopentadienyl proton resonances. Ir(KBr): 1192 (P=O) and 1107, 1010 cm^{-1} (FeC_5H_5). *Anal* Calcd for $C_{26}H_{28}NOPFe$: C, 68.28; H, 6.17; N, 3.06. Found: C, 68.54; H, 6.05; N, 2.92.

(*R*)-1-Diphenylphosphinyl-2-ethylferrocene (8). To a solution of 0.93 g (2.03 mmol) of (*S*)-(*R*)-6 in 45 ml of acetone, 5.0 ml of methyl iodide was added at room temperature. The solution was refluxed for 15 min and concentrated *in vacuo* to *ca.* 15 ml. The residue was diluted with 30 ml of benzene, washed with 50 ml of 8.5% aqueous phosphoric acid and 50 ml of 10% aqueous sodium hydroxide, and dried over anhydrous sodium sulfate. After evaporation of the solvents, the residue was chromatographed on silica gel (eluent benzene/ethyl acetate, 3/1) to give 0.61 g (73%) of crude (*R*)-1-diphenylphosphinyl-2-vinylferrocene (7) as a reddish-brown viscous oil, nmr(CCl_4/TMS): δ 4.12 (s, FeC_5H_3), 4.22 (s, FeC_5H_5), 4.7-5.5 (m, $CH=CH_2$), 5.9-6.7 (m, $CH=CH_2$), and 7.1-7.9 (m, C_6H_5). The ir spectrum indicated the presence of vinyl group (1625 cm^{-1}), phosphinyl group (1193 cm^{-1}), and unsubstituted cyclopentadienyl ring (1108 and 1002 cm^{-1}).

The crude vinylferrocene ((*R*)-7) (0.57 g) in 5 ml of benzene solution was hydrogenated in a 50 ml steel autoclave at 130 kg/cm^2 of hydrogen in the presence of 10 mg of chlorotris(triphenylphosphine)rhodium to give, after chromatography on alumina (elution with benzene/ethyl acetate, 2/1), 0.29 g of (*R*)-8, mp 151.5-152° (in a sealed tube), $[\alpha]_D^{25}$ +118° (*c* 0.62, chloroform), nmr(CCl_4/

TMS): δ 0.95 (t, J = 7.0 Hz, CH_3), 2.26-2.77 (broad m, CH_2), 4.25 (s, FeC_5H_5), 3.72, 4.17, and 4.32 (three broad s, FeC_5H_3), and 7.22-7.96 (m, C_6H_5). The ir spectrum indicated the presence of a phosphinyl group (1190 cm^{-1}) and an unsubstituted cyclopentadienyl ring (1105 and 1000 cm^{-1}). *Anal* Calcd for $C_{24}H_{23}OPFe$: C, 69.58; H, 5.60. Found: C, 69.75; H, 5.61.

(*R*)-1-Diphenylphosphino-2-ethylferrocene (PPEF). A solution of 0.23 g (0.55 mmol) of (*R*)-8 in 5 ml of benzene was added at room temperature to a solution of 0.1 g of lithium aluminum hydride in 4 ml of dry dibutyl ether over a period of 10 min. The reaction mixture was heated at 80-85° for 4.5 hr. After work-up in the usual way, chromatography on alumina using benzene as an eluent gave 0.17 g (78%) of (*R*)-PPEF, uv: $\lambda_{max}(CHCl_3)$ 446 nm (ε 155), nmr(CCl_4/TMS): δ 1.01 (t, J = 7.0 Hz, CH_3), 2.19-2.71 (m, CH_2), 3.94 (s, FeC_5H_5), 3.56, 4.10, and 4.27 (three broad s, FeC_5H_3), and 6.76-7.62 (m, C_6H_5). ORD(σ 0.12 and 0.005, chloroform): $[\Phi]_{589}$ +1080°, $[\Phi]_{474}$ +2450° (pk), $[\Phi]_{428}$ +1880° (tr), and $[\Phi]_{294}$ +14,400° (pk). CD spectrum was shown in Figure 2. *Anal* Calcd for $C_{24}H_{23}PFe$: C, 72.38; H, 5.82. Found: C, 72.36; H, 5.86.

Asymmetric hydrosilylation of ketones

Hydrosilylation was carried out essentially in the same manner as described in Chapter 6. A mixture of di-μ-chlorobis-(1,5-hexadiene)dirhodium(I) with (*S*)-(*R*)-PPFA (phosphine/Rh = 1 or 2), (*R*)-(*S*)-MPFA (phosphine/Rh = 2), (*S*)-(*R*)-BPPFA (diphosphine/Rh = 1), or (*R*)-PPEF (phosphine/Rh = 2) was used as a catalyst precursor. The reaction conditions, yields, and optical yields of the products are summarized in Tables II, III, IV, and V. When α-naphthylphenylsilane was used, silyl ethers were not isolated but converted directly into alkanols by hydrolysis.

REFERENCES AND NOTES

1. A preliminary communication has appeared in Tetrahedron Lett., 4405 (1974).
2. a) W. S. Knowles and M. J. Sabacky, Chem. Commun., 1445 (1968); W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, J. C. S. Chem. Commun., 10 (1972). b) L. Horner, H. Siegel, and H. Büthe, Angew. Chem., 80, 1034 (1968).
3. J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, J. Amer. Chem. Soc., 93, 1301 (1971); see also, J. D. Morrison and W. F. Masler, J. Org. Chem., 39, 270 (1974).
4. T.-P. Dang and H. B. Kagan, Chem. Commun., 481 (1971); *idem*, J. Amer. Chem. Soc., 94, 6429 (1972).
5. a) K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 46, C65 (1972); *idem*, *ibid.*, 54, C45 (1973). b) I. Ojima, T. Kogure, and Y. Nagai, Chem. Lett., 541 (1973); I. Ojima and Y. Nagai, Chem. Lett., 223 (1974). c) W. Dumont, J.-C. Poulin, T.-P. Dang, and H. B. Kagan, J. Amer. Chem. Soc., 95, 8295 (1973). d) R. J. P. Corriu and J. J. E. Moreau, J. Organometal. Chem., 64, C51 (1974).
6. D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, and I. Ugi, J. Amer. Chem. Soc., 92, 5389 (1970).
7. M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Wiley, New York, N. Y., 1965, p. 40.
8. a) Rauchfuss and Roundhill [J. Amer. Chem. Soc., 96, 3098 (1974)] have reported that *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline can make a chelate ring with rhodium using both phosphorus and nitrogen atoms. b) J. C. Kotz, C. L. Nivert, and J. M. Lieber, J. Organometal. Chem., 84, 255 (1975).
9. M. Kumada, Y. Kiso, and M. Umeno, Chem. Commun., 611 (1970); Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, J. Organometal. Chem., 50, 297 (1973).

Chapter 8

Asymmetric Hydrosilylation of α,β-Unsaturated Carbonyl Compounds[1]

SUMMARY

Asymmetric hydrosilylation of (*E*)-4-phenylpent-3-en-2-one and (*E*)-1,3-diphenylbut-2-en-1-one with phenyldimethylsilane or trimethylsilane in the presence of BMPP-Rh^+ or DIOP-Rh as catalyst took place in a 1,4 fashion to afford optically active silyl enol ethers. The silyl enol ethers were converted by hydrolysis into optically active saturated ketones.

The hydrosilylation of β-methylcinnamaldehyde with trialkylsilanes gave not only 1,4-adduct but also 1,2-adduct.

INTRODUCTION

Catalytic hydrosilylation of ketones[2] and imines[3] may be considered as a synthetically equivalent means to the reduction of these compounds. The reaction is of considerable use for enantioselective reduction of C=O[4] or C=N[5] bonds when chiral rhodium complexes are employed as catalysts.

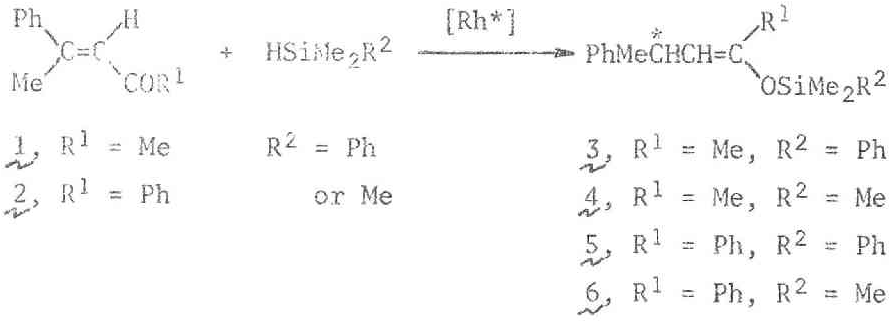
In 1959, Sadykh-Zade and Petrov reported that chloroplatinic acid-catalyzed hydrosilylation of α,β-unsaturated carbonyl compounds takes place in a 1,4 fashion.[6] Recently, Ojima, Kogure, and Nagai have found that highly selective 1,2- as well as 1,4-addition of hydrosilanes to α,β-unsaturated terpene ketones can be achieved, the selectivity depending markedly on the nature of the hydrosilane employed.[7]

As an extention of the studies on the asymmetric hydro-

silylation of olefins[8] and ketones[4a] catalyzed by Group VIII transition metal complexes with chiral phosphine ligands, we describe, in this chapter, the asymmetric 1,4-addition of hydrosilanes to α,β-unsaturated ketones using chiral phosphine-rhodium complexes as catalysts.

RESULTS AND DISCUSSION

We have found that the chiral cationic complex, $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (S = solvent),[4a] prepared *in situ*, catalyzes the asymmetric hydrosilylation of α,β-unsaturated ketones under mild conditions. ((-)-DIOP)Rh(S)Cl,[4c] where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane, was also used in the present reactions.



1, R^1 = Me; 2, R^1 = Ph

R^2 = Ph or Me

3, R^1 = Me, R^2 = Ph
4, R^1 = Me, R^2 = Me
5, R^1 = Ph, R^2 = Ph
6, R^1 = Ph, R^2 = Me

(1)

7, R^1 = Me
8, R^1 = Ph

[Rh*] = $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (abbr. BMPP-Rh^+)
((-)-DIOP)Rh(S)Cl (abbr. DIOP-Rh)

Thus, addition of phenyldimethylsilane to (*E*)-4-phenylpent-3-en-2-one (1) in the presence of BMPP-Rh^+ dissolved in benzene at room temperature gave only a 1,4-adduct, 2-phenyldimethylsiloxy-4-phenylpent-2-ene (3), α_D^{20} -0.68° (0.1 dm, neat), in 76% yield. Hydrolysis of 3 with potassium hydroxide in aqueous methanol gave 4-phenylpentan-2-one (7),[9,10] $[\alpha]_D^{20}$ -5.31°(neat). Hydrosilylation of 1 with trimethylsilane produced, after hydrolysis, the same saturated ketone (7) of lower optical activity.

Hydrosilylation was also carried out with (*E*)-1,3-diphenylbut-2-en-1-one (2) in the presence of BMPP-Rh^+ or DIOP-Rh to give optically active 1-phenyldimethylsiloxy-1,3-diphenylbut-1-ene (5) or its trimethylsiloxy analog (6), respectively. 5 and 6 were converted by hydrolysis into 1,3-diphenylbutan-1-one (8).[11]

7 and 8 were converted *via* Baeyer-Villiger oxidation into 2-phenylpropanol (10)[9,12] and 3-phenylbutanol (12)[13,14] in order to confirm optical purity (eq. 2 and 3).

$$\underset{\underset{7,\ [\alpha]_D^{25}\ -5.31°}{}}{PhMe\overset{*}{C}HCH_2COMe} \xrightarrow[CHCl_3]{PhCO_3H} \underset{9}{PhMe\overset{*}{C}HCH_2OCOMe} \xrightarrow{KOH/H_2O} \underset{10,\ [\alpha]_D^{20}\ -2.14°}{PhMe\overset{*}{C}HCH_2OH} \quad (2)$$

$$\underset{\underset{8,\ [\alpha]_D^{25}\ -1.47°}{}}{PhMe\overset{*}{C}HCH_2COPh} \xrightarrow[CHCl_3]{PhCO_3H} \underset{11}{PhMe\overset{*}{C}HCH_2CO_2Ph} \xrightarrow[Et_2O]{LiAlH_4} \underset{12,\ [\alpha]_D^{25}\ -3.94°}{PhMe\overset{*}{C}HCH_2CH_2OH} \quad (3)$$

The results obtained for the asymmetric hydrosilylation of α,β-unsaturated ketones are summarized in Table I. It is noted that in all cases BMPP-Rh^+ or DIOP-Rh catalyzes the addition reaction to give (*R*)-ketones preferentially, that is, the addition in a sense of selecting a *si-si* face of carbon-carbon double bonds of α,β-unsaturated ketones in an *E* form whether R^1 is

Table I. Asymmetric Hydrosilylation of α,β-Unsaturated Ketones Catalyzed by Chiral Phosphine-Rhodium Complexes.[a,b]

R^1	R^2	Catalyst	Yield (%)	Silyl enol ether α_D^{20} (0.1 dm, neat)	Ketone $[\alpha]_D^{25}$	Configuration	Optical[c] yield (%)
Me	Ph	BMPP-Rh^+	76	-0.680	-5.31[d]	*R*	15.6[e]
Me	Ph	DIOP-Rh	92	-0.356		*R*	6.4
Me	Me	BMPP-Rh^+	90	-0.153	-0.47[d]	*R*	1.4[e]
Ph	Ph	BMPP-Rh^+	72	-2.62[f]		*R*	10.0[e]
Ph	Ph	DIOP-Rh	83	-1.09[f]	-0.48[g]	*R*	3.3
Ph	Me	BMPP-Rh^+	94	-0.123	-1.09[g]	*R*	9.5[e]
Ph	Me	DIOP-Rh	87	-0.162	-1.47[g]	*R*	10.1

[a] [Rh*] = 0.1 mol%. [b] The reaction of 1 and 2 was carried out at room temperature and at 50°, respectively. [c] On the basis of the optical purity of 10 and 8. [d] Neat. [e] Calibrated for the optical purity of the chiral phosphine used (79%). [f] Specific rotation in benzene (*c* 10). [g] Specific rotation in carbon tetrachloride (*c* 5).

methyl or phenyl group.

Attempted asymmetric hydrosilylation of β-methylcinnamaldehyde (13) with trimethylsilane resulted in giving not only a 1,4-adduct, 1-trimethylsiloxy-3-phenylbut-1-ene (14), but also a 1,2-adduct, 1-trimethylsiloxy-3-phenylbut-2-ene (16); the glc ratio of 14 to 16 was 64/36. Both 1,4-adduct (15) and 1,2-adduct (17) (59/41) were also formed from the reaction with phenyldimethylsilane (eq. 4). However, 14 and 15 were obtained in an optically inactive form.

$$\underset{\underset{13}{}}{\text{PhMeC=CHCHO}} \xrightarrow[\text{DIOP-Rh, } 0^\circ]{\text{HSiMe}_2\text{R}^2} \underset{\underset{14,\ R^2 = Me}{\underset{15,\ R^2 = Ph}{}}}{\text{PhMeCHCH=C}\begin{matrix}\diagup\ \text{OSiMe}_2\text{R}^2 \\ \diagdown\ \text{H}\end{matrix}} + \underset{\underset{16,\ R^2 = Me}{\underset{17,\ R^2 = Ph}{}}}{\text{PhMeC=C}\begin{matrix}\diagup\ \text{CH}_2\text{OSiMe}_2\text{R}^2 \\ \diagdown\ \text{H}\end{matrix}} \qquad (4)$$

Of particular significance is that the present reaction may provide a facile route to the preparation of optically active silyl enol ethers, which are well suited for generation of metal enolate species.[15]

EXPERIMENTAL

The preparation of BMPP-Rh* and DIOP-Rh was described in Chapter 6.

Asymmetric hydrosilylation of α,β-unsaturated ketones

1. (*E*)-4-phenylpent-3-en-2-one (1).

(a) With phenyldimethylsilane. The following procedure for

an asymmetric hydrosilylation of 1 is typical. In a degassed sealed glass tube, a mixture of 4.8 g (30 mmol) of 1, 4.1 g (30 mmol) of phenyldimethylsilane, and 3×10^{-2} mmol of BMPP-Rh^+ (with the phosphine of 79% optical purity) dissolved in 3 ml of benzene was allowed to stand at room temperature over a period of 40 hr. The product was isolated by distillation through a short Vigreux column to give 6.7 g (76%) of 2-phenyldimethylsiloxy-4-phenylpent-2-ene (3), bp 121-123° (0.04 mm), α_D^{20} -0.680° (0.1 dm, neat). 3 was found to consist of (*Z*)- and (*E*)-isomers in a ratio of 80:20 on the basis of nmr analysis, nmr(CCl_4/TMS): (*Z*)-3; δ 0.41 (s, $SiCH_3$), 1.22 (d, J = 7.6 Hz, $CHCH_3$), 1.69 (s, $=CCH_3$), 3.2-4.0 (m, $CHCH_3$), 4.45-4.85 (m, $=CH$), and 6.9-7.6 (m, CC_6H_5 and SiC_6H_5). (*E*)-3; δ 0.36 (s, $SiCH_3$) and 1.81 (broad s, $=CCH_3$), and other signals are indistinguishable from those of (*Z*)-3. *Anal* Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.30; H, 8.13.

To a solution of 6.2 g (21 mmol) of (*E*)- and (*Z*)-3 thus obtained in 30 ml of methanol, 20 ml of 2 *N* potassium hydroxide was added dropwise with stirring at room temperature. The hydrolysis was completed within 10 min. The organic products were extracted with ether and this ether extract was dried over sodium sulfate. After evaporation of ether, distillation gave almost quantitatively 4-phenylpentan-2-one (7), d_4^{20} 0.9763, $[\alpha]_D^{20}$ -5.31° (neat), -6.8° (*c* 4, benzene), (lit.[10] maximum rotation: $[\alpha]_D^{20}$ -74.5° (*c* 1, benzene), see also note 9).

The results of asymmetric hydrosilylation of 1 using DIOP-Rh as catalyst are listed in Table I.

(b) With trimethylsilane. From a mixture of 4.8 g (30 mmol) of 1, 2.2 g (30 mmol) of trimethylsilane, and 3×10^{-2} mmol of BMPP-Rh^+ dissolved in 3 ml of benzene, was obtained 6.3 g (90%) of 2-trimethylsiloxy-4-phenylpent-2-ene (4), bp 78-79° (2.5 mm), α_D^{20} -0.153° (0.1 dm, neat). 4 was shown to consist of (*Z*)- and (*E*)-isomers (60:40) on the basis of nmr analysis, nmr(CCl_4/TMS): (*Z*)-4; δ 0.16 (s, $SiCH_3$), 1.29 (d, J = 6.4 Hz, $CHCH_3$), 1.70 (s,

=CCH_3), 3.2-3.9 (m, CHCH$_3$), 4.4-4.9 (m, =CH), and 7.16 (s, C$_6H_5$). (*E*)-4; δ 0.13 (s, SiCH_3), 1.23 (d, J = 6.4 Hz, CHCH_3), and 1.75 (s, =CCH_3), and other signals are indistinguishable from those of (*Z*)-4. *Anal* Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 70.86; H, 9.32.

4 was hydrolyzed with potassium hydroxide in aqueous methanol to give 7, $[\alpha]_D^{20}$ -0.47° (neat).

2. (*E*)-1,3-diphenylbut-2-ene-1-one (2)

(a) With phenyldimethylsilane. A mixture of 8.9 g (40 mmol) of 2, 5.5 g (40 mmol) of phenyldimethylsilane, and 4×10^{-2} mmol of DIOP-Rh dissolved in 5 ml of benzene was heated at 50° for 40 hr. Distillation gave 12.0 g (83%) of (*Z*)-1-phenyldimethylsiloxy-1,3-diphenylbut-1-ene (5), bp 180-185° (0.2 mm), $[\alpha]_D^{20}$ -1.09° (*c* 10, benzene), nmr(CCl$_4$/TMS): δ 0.32 (s, SiCH_3), 1.23 (d, J = 7.2 Hz, CHCH_3), 3.56-4.06 (double q centered at 3.78, CHCH$_3$), 5.24 (d, J = 9.6 Hz, =CH), and 6.9-7.6 (m, C$_6H_5$). *Anal* Calcd for $C_{24}H_{26}OSi$: C, 80.40; H, 7.31. Found: C, 80.20; H, 7.47.

5 was hydrolyzed with potassium hydroxide in aqueous methanol to give quantitatively 8, $[\alpha]_D^{20}$ -0.48° (*c* 5, carbon tetrachloride), (lit.[11] (*R*)-8 has $[\alpha]_D$ -14.6° (*c* 1.8, carbon tetrachloride)).

(b) With trimethylsilane. Similarly but with 3.0 g (40 mmol) of trimethylsilane, 10.3 g (87%) of (*Z*)-1-trimethylsiloxy-1,3-diphenylbut-1-ene (6), bp 145-149° (3 mm), α_D^{20} -0.162° (0.1 dm, neat) was obtained. Nmr(CCl$_4$/TMS): δ 0.07 (s, SiCH_3), 1.36 (d, J = 6.6 Hz, CHCH_3), 3.6-4.2 (double q, CHCH$_3$), 5.27 (d, J = 9.4 Hz, =CH), and 7.0-7.5 (m, C$_6H_5$). *Anal* Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.73; H, 8.37.

6 was hydrolyzed to give quantitatively 8, $[\alpha]_D^{20}$ -1.47° (*c* 5, carbon tetrachloride), $[\alpha]_D^{25}$ -2.54° (*c* 5, benzene).

The results using BMPP-Rh$^+$ as catalyst are listed in Table I.

Oxidation of ketones

1. 4-Phenylpentan-2-one (7). To a solution of 1.7 g of 7 ($[\alpha]_D^{20}$ -5.31° (neat)) in 5 ml of chloroform, 30 ml of 1.0 *N* perbenzoic acid in chloroform was added. After standing in the dark at room temperature for 3 months, the mixture was extracted with 10% sodium hydroxide. The extract was washed with water, and concentrated *in vacuo* to give crude 2-phenylpropyl acetate (9). The ester (9) was saponified by refluxing for 30 min with 8 ml of 50% ethanol-water containing 1.0 g of potassium hydroxide. The hydrolysis mixture was worked up to yield 1.0 g (71%) of 2-phenylpropanol (10), $[\alpha]_D^{20}$ -2.14° (neat), which was determined to be of 12.3% enantiomeric excess of the *S* isomer on the basis of the known value[12] of $[\alpha]_D^{15}$ -17.4° (neat) for optically pure (*S*)-10.

2. 1,3-Diphenylbutan-1-one (8). Similarly, 8 (4.5 g, 20 mmol) ($[\alpha]_D^{20}$ -1.47° (*c* 5, carbon tetrachloride)) was treated with perbenzoic acid in chloroform solution to give crude phenyl β-phenylbutyrate (11). The crude ester (11) was reduced with 2.5 g of lithium aluminum hydride in 10 ml of ether. After work-up, preparative glc (Silicone DC550) gave 1.6 g (53%) of 3-phenylbutanol (12), $[\alpha]_D^{20}$ -3.94° (neat), (lit.[13] (*R*)-12 has $[\alpha]_D$ -39.56° (neat)).

Hydrosilylation of β-methylcinnamaldehyde (13)

1. With trimethylsilane. In a degassed sealed glass tube, a mixture of 4.4 g (30 mmol) of 13 (a mixture of (*E*)- and (*Z*)-isomers (*ca.* 1:1)), 2.2 g (30 mmol) of trimethylsilane, and 3×10^{-2} mmol of DIOP-Rh dissolved in 4.0 ml of benzene was kept at 0° for 24 hr. Distillation gave 4.5 g (68% combined yield) of a mixture, boiling over a range of 71-78° (2 mm), of (*E*)-1-trimethylsiloxy-3-phenylbut-1-ene (14), (*Z*)-14, (*E*)-1-trimethylsiloxy-3-phenylbut-2-ene (16), and (*Z*)-16. The glc area ratio of the products was 44:20:15:21, respectively. All these com-

pounds were isolated by preparative glc (Silicone DC550) and characterized by ^{1}H nmr spectra, nmr(CCl_4/TMS): (*E*)-14; δ 0.17 (s, $SiCH_3$), 1.32 (d, J = 6.6 Hz, CCH_3), 3.32 (5, $CHCH_3$), 5.07 (double d, J = 12.0 and 7.8 Hz, =C*H*C), 6.13 (d, J =12.0 Hz, =C*H*O), and 7.11 (s, C_6H_5). (*Z*)-14; δ 0.14 (s, $SiCH_3$), 1.23 (d, J = 6.8 Hz, $CHCH_3$), 3.35 (5, $CHCH_3$), 4.56 (double d, J = 6.0 and 9.2 Hz, =C*H*C), 5.99 (d, J = 6.0 Hz, =C*H*O), and 7.10 (s, C_6H_5). (*E*)-16; δ 0.14 (s, $SiCH_3$), 2.01 (broad s, CCH_3), 4.27 (d, J =6.2 CH_2), 5.78 (t, =C*H*), and 7.21 (broad s, C_6H_5). (*Z*)-16; δ 0.13 (s, $SiCH_3$), 2.04 (s, CCH_3), 3.91 (d, J = 6.2 Hz, CH_2), 5.51 (t, =C*H*), and 7.14 (broad s, C_6H_5). The mixture of 14 and 16, α_D^{20} 0.00° (0.1 dm, neat). *Anal* Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 69.82; H, 9.22.

(*E*)- and (*Z*)-14 were hydrolyzed with potassium hydroxide in aqueous methanol to give 3-phenylbutanal. It was optically inactive.

2. With phenyldimethylsilane. Similarly, from a mixture of 4.8 g (30 mmol) of 13, 4.1g (30 mmol) of phenyldimethylsilane, and 3×10^{-2} mmol of DIOP-Rh, was obtained 6.8 g (70% combined yield) of addition products, which boiled over a range of 103-126° (0.02 mm). Nmr indicated that the mixture consists of (*E*)- and (*Z*)-1-phenyldimethylsiloxy-3-phenylbut-1-ene (15) and (*E*)- and (*Z*)-1-phenyldimethylsiloxy-3-phenylbut-2-ene (17) in a ratio of 59:41, nmr(CCl_4/TMS): (*E*)-15; δ 1.28 (d, J = 6.8 Hz, $CHCH_3$), 5.10 (double d, J = 12.0 and 7.6 Hz, =C*H*C), (*Z*)-15; 1.26 (d, J = 6.8 Hz, $CHCH_3$), 4.60 (double d, J = 6.0 and 9.0 Hz, =C*H*C), (*E*)- and (*Z*)-17; 1.91, 2.05 (s, CCH_3), and 3.98, 4.26 (d, CH_2), and other overlapping signals could not be assigned. The mixture of 15 and 17 had no optical activity. *Anal* Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 75.76; H, 8.10.

1. A preliminary communication has appeared in Tetrahedron Lett., 3 (1975).
2. a) I. Ojima, M. Nihonyanagi, and Y. Nagai, Chem. Commun., 938 (1972). b) I. Ojima, T. Kogure, M. Nihonyanagi. and Y. Nagai, Bull. Chem. Soc. Japan, 45, 3506 (1972). c) R. J. P. Corriu and J. J. E. Moreau, Chem. Commun., 38 (1973).
3. I. Ojima, T. Kogure, and Y. Nagai, Tetrahedron Lett., 2475 (1973).
4. a) K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 46, C65 (1972); *idem, ibid.*, 54, C45 (1973); T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 4405 (1974). b) I. Ojima, T. Kogure, and Y. Nagai, Chem. Lett., 541 (1973); I. Ojima and Y. Nagai, *ibid.*, 223 (1974); I. Ojima, T. Kogure, and Y. Nagai, Tetrahedron Lett., 1889 (1974). c) W. Dumont, J.-C. Poulin, T.-P. Dang, H. B. Kagan, J. Amer. Chem. Soc., 95, 8295 (1973). d) R. J. P. Corriu and J. J. E. Moreau, J. Organometal. Chem., 64, C51 (1974).
5. N. Langlois, T.-P. Dang, and H. B. Kagan, Tetrahedron Lett., 4865 (1973).
6. S. I. Sadykh-Zade and A. D. Petrov, Zh. Obshch. Khim., 29, 3194 (1959) [Chem. Abstr., 54, 12978 (1960)].
7. I. Ojima, T. Kogure, and Y. Nagai, Tetrahedron Lett., 5035 (1972).
8. K. Yamamoto, T. Hayashi, and M. Kumada, J. Amer. Chem. Soc., 93, 5301 (1971); K. Yamamoto, Y. Uramoto, and M. Kumada, J. Organometal. Chem., 31, C9 (1971).
9. Cookson and Kemp have reported[10] the specific rotation of optically pure 7 to be $[\alpha]_D$ -74.5° (*c* 1, benzene). The value, however, is inconsistent with that correlated with optical purity of the alcohol 10 (*cf.* ref. 14).
10. R. C. Cookson and J. E. Kemp, Chem. Commun., 385 (1971).

11. T. L. Leitereg and D. J. Cram, J. Amer. Chem. Soc., 90, 4011 (1968).
12. S. P. Bakshi and E. E. Turner, J. Chem. Soc., 171 (1961).
13. H. Rupe and F. van Walraven, Helv. Chim. Acta, 13, 361 (1930).
14. This conversion indicates that the optical purity of the ketone 8 corresponds exactly with that of the alcohol 12.
15. G. Stork and P. F. Hudrlik, J. Amer. Chem. Soc., 90, 4462 (1968).

Chapter 9

Asymmetric Synthesis of Bifunctional Organosilicon Compounds *via* Hydrosilylation[1]

SUMMARY

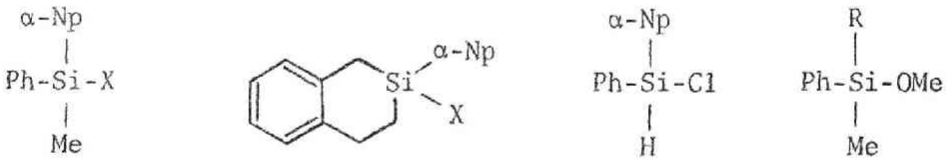
Optically active bifunctional alkoxysilanes were obtained by the addition reaction of methyl-α-naphthylsilane (5a) and α- naphthylphenylsilane (5b) to such symmetric ketones as diethyl ketone and benzophenone in the presence of $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2\text{-}H_2S_2]^+ClO_4^-$ (S = solvent), ((-)-DIOP)Rh(S)Cl, or ((*S*)-(*R*)-BPPFA)-Rh(S)Cl as catalyst. The alkoxysilanes were readily correlated with known methyl-α-naphthylphenylsilane (1a). In this reaction 5a always gave rise to (*R*)-1a in excess, while 5b predominantly to (*S*)-1a.

The reaction of 5a and 5b with aldehydes also gave bifunctional alkoxysilanes, though their optical purity was negligible.

INTRODUCTION

The fundamental work of Sommer and his coworkers on the stereochemistry of organosilicon compounds[2] has originated from the preparation of optically pure methyl-α-naphthylphenylsilane (1a) and closely related compounds, which are obtained *via* fractional crystallization of diastereomeric menthoxymethyl-α-naphthylphenylsilane (1b). Another system having asymmetric silicon —— cyclic one (2) —— has been developed by Corriu *et al.*[3] using a similar technique as a probe of a different stereochemistry of some substitution reactions at silicon.

However, few examples of the preparation of optically active organosilanes by asymmetric synthesis or by kinetic resolution have been recorded so far in the literature. Corriu *et al.*[4] have reported a kinetic resolution of bifunctional organosilanes during menthanolysis of chloro-α-naphthylphenylsilane (3), the latter being assumed to undergo extensive racemization under the conditions employed. Recently, Holt and coworkers[5] have carried out partial reduction of various racemic methoxysilanes (4, R = α-naphthyl, ethyl, and benzyl) by a chiral reducing complex of lithium aluminum hydride to achieve a kinetic resolution.



1 a: X = H
b: X = OMen

2

3

4

The only asymmetric synthesis at a silicon center has been ovserved by Klebe *et al.*[6] in the reaction of bis(*N*-methylacetamido)-methylphenylsilane with optically active amino acids to form unequal amounts of diastereomeric pairs of 2-siloxazolidone-5, which are claimed to undergo a second order asymmetric transformation. To our best knowledge, however, there are no data of asymmetric induction at a prochiral silicon center in a sense of catalytic asymmetric reactions, on which increasing attention has been focused recently.

In the preceding chapters we have described that chiral phosphine-rhodium complexes are effective to cause stereoselective addition of a hydrosilane to a variety of prochiral carbonyl compounds to give silyl ethers of the corresponding alkanols with fairly high enantiomeric bias at the carbon atom.[7,8] The present chapter describes an application of the catalytic asymmetric

hydrosilylation of ketones to the preparation of some new asymmetric bifunctional organosilanes.

After our investigation had been completed, Corriu *et al.* reported independently that alcoholysis of α-naphthylphenylsilane or addition reaction of the silane to ketones both catalyzed by (+)- or (-)-DIOP-rhodium complex leads to an optically active alkoxysilane.[9]

RESULTS AND DISCUSSION

$[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ [7a] (S = solvent), ((-)-DIOP)Rh(S)Cl,[10] where (-)-DIOP stands for (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, and ((*S*)-(*R*)-BPPFA)Rh(S)Cl,[7b] where (*S*)-(*R*)-BPPFA stands for (*S*)-α-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]ethyldimethylamine, were used as catalysts for the present reactions. These complexes have been effectively used for asymmetric hydrosilylation of prochiral ketones.[7]

Addition of certain dihydrosilane, $H_2SiR^1R^2$, having a *meso*-silicon atom to such symmetric ketones as diethyl ketone and benzophenone in the presence of the chiral phosphine-rhodium complexes gave silyl ethers in the optically active form associated with the silicon atom (eq. 1).[11,14]

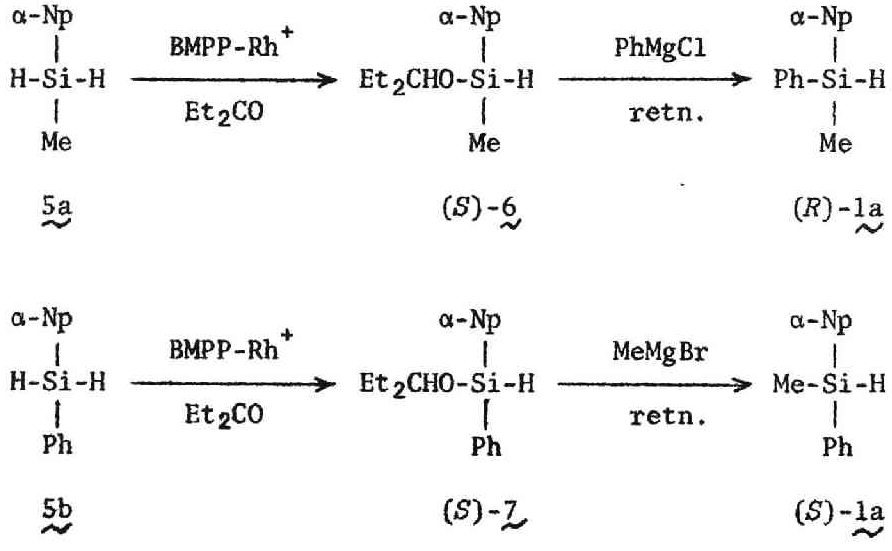
$$R_2CO + H_2SiR^1R^2 \xrightarrow{[Rh]^*} R_2CH\overset{*}{O}SiHR^1R^2 \qquad (1)$$

R_2 = Me_2, Et_2, $-(CH_2)_5-$, and Ph_2; R^1 = Me and Ph; R^2 = α-Np

[Rh]* = $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (abbr. BMPP-Rh^+)
((-)-DIOP)Rh(S)Cl (abbr. DIOP-Rh)
((*S*)-(*R*)-BPPFA)Rh(S)Cl (abbr. BPPFA-Rh)

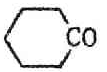
The silyl ethers were converted into known methyl-α-naphthylphenylsilane (1a) in order to examine respective optical yields, although such conversion may be accompanied by considerable racemization.[15]

The results obtained for the reaction catalyzed by BMPP-Rh^+ are summarized in Table I. It is noteworthy that one enantiomer of 1a was produced in excess through the hydrosilylation of ketones using methyl-α-naphthylsilane (5a) while the other enantiomer was obtained in excess starting with α-naphthylphenylsilane (5b). If, for example, phenylation of 3-pentyloxy-α-naphthylmethylsilane (6) and methylation of 3-pentyloxy-α-naphthylphenylsilane (7) proceed largely with retention of configuration at the silicon center,[4,15] the following scheme would be valid to rationalize the present results. This clearly suggests that, in both cases of forming 6 and 7, one enantiotopic hydrogen (*pro S*) attached to the silicon atom of the dihydrosilanes (5a and 5b) participates preferentially in the chiral complex-catalyzed hydrosilylation of symmetric ketones over the other (*pro R*).



Scheme I.

Table I. Asymmetric Induction at a *meso*-Silicon Atom *via* Hydrosilylation of Ketones Catalyzed by BMPP-Rh$^+$ at Room Temperature.

Ketone	Silyl ether $[\alpha]_D^{20}$ (neat)	Yield (%)	α-NpPhMeSiH (1a)[a] $[\alpha]_D^{20}$ (cyclohexane)	Optical yield[b] (%) (Configuration)
α-NpMeSiH$_2$ (5a)				
Me_2CO	-2.31	63	+2.05	7.4 (*R*)
Et_2CO	-4.40	69	+2.38	8.6 (*R*)
	-3.30	81	+2.02	7.2 (*R*)
Ph_2CO	-4.33[c]	72	+5.45	19.7 (*R*)
α-NpPhSiH$_2$ (5b)				
Me_2CO	-0.09	76	-0.14	— (*S*)
Et_2CO	-0.57	86	-1.98	7.2 (*S*)
	-0.92	72	-0.86	3.1 (*S*)
Ph_2CO	—	—	-7.66	27.7 (*S*)

[a] Optically pure (*R*)-α-NpPhMeSiH, $[\alpha]_D$ +35.0° (*c* 15.6, cyclohexane). [b] Calibrated on the basis of the optical purity of phosphine used (79%). [c] Measured in cyclohexane.

There is solid evidence that the oxidative addition of an optically active hydrosilane, *e.g.* 1a, to an appropriate platinum complex proceeds with retention of configuration.[16] The implication is that the configurational stability around a silicon atom during the activation of a dihydrosilane by the catalyst may play an important role to exert asymmetric induction at the *meso*-silicon atom.[17]

A considerable variation of optical yields on changing ketone structure should also be mentioned (Table I); benzophenone gave appreciably higher optical yield than other ketones in the reaction of both 5a and 5b. The extent of asymmetric induction would principally be determined during the oxidative addition of one of two enantiotopic hydrogen-silicon bonds in a *meso*-dihydrosilane to the rhodium complex with chiral phosphines as ligands, prior to the successive insertion of the ketone carbonyl to the resulting silicon-rhodium moiety and reductive elimination of the silyl ether (as to the mechanism of hydrosilylation of ketones, see Chapter 6). However, it seems reasonable that the difference in bulkiness of the ketone, which is coordinated to the chiral phosphine-rhodium complex like solvent, must influence the stereoselectivity to some extent because of modifying the effective bulk of the rhodium complex. Then, benzophenone is of advantage for attaining higher asymmetric induction than the less bulky ketones.

In DIOP-Rh and BPPFA-Rh catalyst systems, it was also found that the addition of 5a to symmetric ketones always affords (*R*)-1a in excess after phenylation of the resulting silyl ethers, while 5b leads to (*S*)-1a (Table II). Considerably high optical yields were obtained in the reaction of 5b catalyzed by DIOP-Rh. This is the very case reported by Corriu and coworkers.[9b]

The fact that 5a always resulted in the formation of (*R*)-1a and 5b in (*S*)-1a regardless of different chiral phosphine-rhodium complexes as catalysts is only fortuitous. However, 5a and 5b

Table II. Asymmetric Induction at a *meso*-Silicon Atom *via* Hydrosilylation of Ketones Catalyzed by DIOP-Rh and BPPFA-Rh at Room Temperature.

Silane	Ketone	α-NpPhMeSiH (1a) $[\alpha]_D^{20}$ (cyclohexane)	Optical yield (%) (Configuration)
Catalyst: DIOP-Rh			
α-NpMeSiH$_2$	Et_2CO	0	—
α-NpMeSiH$_2$	Ph_2CO	+6.59	18.8 (*R*)
α-NpPhSiH$_2$	Et_2CO	-18.50	52.9[a] (*S*)
α-NpPhSiH$_2$	Ph_2CO	-16.05	45.9[b] (*S*)
Catalyst: BPPFA-Rh			
α-NpMeSiH$_2$	Et_2CO	+1.07	3.1 (*R*)
α-NpPhSiH$_2$	Et_2CO	-2.67	7.6 (*S*)
α-NpPhSiH$_2$	Ph_2CO	-3.40	9.7 (*S*)

[a,b] Corriu *et al.* have reported that the same reaction but with (+)-DIOP-rhodium complex gives the optical yield of 46% (*R*) and 31% (*R*), respectively (ref. 9b).

do react by using one (*pro-S*) of two enantiotopic hydrogens available to lead necessarily 1a to an opposite enantiomeric bias to each other, reflecting that the α-naphthyl group is always operative as a larger substituent of the dihydrosilanes than the methyl or phenyl one in the present reactions.

The addition reaction of 5a or 5b to a few aldehydes in the presence of BMPP-Rh$^+$ was also examined (eq. 2). The reaction gave the silyl ethers of primary alkanols in moderate yields without deactivation of the catalyst owing to a possible side reaction such as decarbonylation.[18] No appreciable asymmetric induction, however, was observed as shown in Table III.

Table III. Asymmetric Induction at *meso*-Silicon Atom *via* Hydrosilylation of Aldehydes Catalyzed by BMPP-Rh^+ at Room Temperature.

Aldehyde	Silyl ether $[\alpha]_D^{20}$ (neat)	Yield (%)	α-NpPhMeSiH $[\alpha]_D^{20}$[a]	Optical yield (%) (Configuration)
α-$NpMeSiH_2$ (5a)				
MeCHO	-0.04	74	0	—
PhCHO	0	78	0	—
α-$NpPhSiH_2$ (5b)				
PhCHO	-0.24[a]	56	-0.08	0.3 (*S*)

[a] Measured in cyclohexane.

$$RCHO + H_2SiR^1R^2 \xrightarrow{BMPP\text{-}Rh^+} RCH_2OSiHR^1R^2 \qquad (2)$$

R = Me and Ph; R^1 = Me and Ph; R^2 = α-Np

On this basis it may be concluded that the relative bulkiness of the carbonyl compounds, which are coordinated to the rhodium catalyst, exerts a critical effect on selecting one enantiotopic hydrogen-silicon bond of the dihydrosilanes (5a and 5b) to be activated by the catalyst.

EXPERIMENTAL

Optical rotations were measured with a Yanagimoto OR-50 polarimeter. $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$, ((-)-DIOP)Rh(S)Cl, and ((*S*)-(*R*)-BPPFA)Rh(S)Cl were prepared as described in Chapters 6 and 7.

Table IV. Physical Constants and Analytical Data for Hydrosilylation Products

Compound	bp (°C/mm)	n_D^{20}	d_4^{20}	C(%) Found(Calcd.)	H(%) Found(Calcd.)
α-NpMeSiH(OCHR^{1}R^2)					
R^1 R^2					
Me Me	117/4	1.5574	1.0072	73.25(72.99)	8.17(7.88)
Et Et	157/6	1.5501	0.9929	74.13(74.36)	8.38(8.58)
$+CH_2+_5$	141/0.1	1.5711	1.0412	75.52(75.50)	8.32(8.20)
Ph Ph	208/0.07	—	—	81.26(81.31)	6.23(6.25)
Me H	101/2.5	1.5703	1.0247	72.33(72.17)	7.59(7.45)
Ph H	164/2.5	1.5983	1.0821	77.42(77.65)	6.82(6.52)
α-NpPhSiH(OCHR^{1}R^2)					
R^1 R^2					
Me Me	177/0.5	1.5972	1.0578	78.08(78.03)	6.75(6.89)
Et Et	162/0.05	1.5879	1.0427	78.54(78.70)	7.83(7.55)
$+CH_2+_5$	186/0.09	1.6018	—	79.56(79.47)	7.53(7.28)
Ph Ph	250-60/0.2	—	—	83.71(83.61)	5.79(5.81)
Ph H	193/0.05	—	—	80.93(81.13)	6.02(5.92)

Table V. Ir[a] and ^{1}H Nmr[b] Spectral Data for α-NpMeSiH(OCHR^{1}R^2).

R^1	R^2	Ir(cm^{-1}) ν(SiH)	^{1}H Nmr(δ) $SiCH_3$	SiH[c]	Others[d]
Me	Me	2120	0.53(d)	5.33(q)	1.11(d, J = 6.0 Hz, CCH_3[e]) 1.19(d, J = 6.0 Hz, CCH_3[e]) 4.02(7, J = 6.0 Hz, OCH)
Et	Et	2110	0.55(d)	5.34(q)	0.92(t, J = 6.8 Hz, CH_2CH_3) 1.16-1.85(m, CH_2CH_3) 3.59(5, J = 5.9 Hz, OCH)
$+CH_2+_5$		2110	0.55(d)	5.41(q)	0.9-2.1(broad m, $+CH_2+_5$) 3.46-3.95(broad m, OCH)
Ph	Ph	2120	0.51(d)	5.32(q)	5.77(s, OCH) 7.17(s, C_6H_5[f]) 7.24(s, C_6H_5[f])
Me	H	2120	0.53(d)	5.30(q)	1.22(t, J = 6.8 Hz, CH_2CH_3) 3.73(q, CH_2CH_3)
Ph	H	2120	0.54(d)	5.38(q)	4.71(s, CH_2), 7.21(s, C_6H_5)

[a] Recorded on a Hitachi EPI-G3 grating spectrophotometer. [b] Recorded on a Varian EM-360 spectrometer in carbon tetrachloride solution with tetramethylsilane as internal standard. [c] J(HSi-CH_3) = 2.6-3.0 Hz. [d] α-Np: δ 7.2-8.4 ppm (diffused multiplet). [e] Diastereotopic methyls. [f] Diastereotopic phenyls.

Asymmetric induction at a *meso*-silicon atom *via* hydrosilylation

The reaction conditions, yields, and optical data of the products are summarized in Tables I, II, and III. Some physical constants, analytical data, and infrared [ν(SiH)] and nmr spectral data for the silyl ethers are listed in Tables IV, V, and VI.

Table VI. Ir and ^{1}H Nmr Spectral Data for α-NpPhSiH($\mathrm{HR^1R^2}$)

R^1	R^2	Ir(cm^{-1}) ν(SiH)	^{1}H Nmr(δ) Si*H*	Others[a]
Me	Me	2110	5.72(s)	1.19(d, *J* = 6.8 Hz, CH_3[b])
				1.26(d, *J* = 6.8 Hz, CH_3[b])
				4.17(7, OC*H*)
Et	Et	2110	5.90(s)	0.44-1.12(double t, CH_3)
				1.17-1.77(m, CH_2)
				3.82(5, *J* = 6.6 Hz, OC*H*)
$+CH_2\rightarrow_5$		2115	5.73(s)	0.82-2.06(broad m, $+CH_2\rightarrow_5$
				3.55-4.07(broad m, OC*H*)
Ph	Ph	2120	5.85(s)	5.68(s, OC*H*)
				6.20-6.28(m, C_6H_5)
Ph	H	2120	5.76(s)	4.82(s, CH_2)
				7.21(s, C_6H_5)

[a] α-Np and Ph-Si: δ 7.1-8.3 ppm (diffused multiplet).
[b] Diastereotopic methyls.

1. Reaction of methyl-α-naphthylsilane (5a). The following procedure for an asymmetric addition reaction of 5a to benzophenone is typical. In a degassed sealed glass tube a mixture of 5.2 g (30 mmol) of 5a, 5.5 g (30 mmol) of benzophenone, and 3×10^{-1} mmol of $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (the phosphine of 79% optical purity) dissolved in 3 ml of benzene was allowed to stand at room temperature for 40 hr. The reaction mixture was distilled under reduced pressure to give 7.7 g (72% yield) of benzhydryloxy-α-naphthylmethylsilane (8), bp 208° (0.07 mm), $[\alpha]_D^{20}$ -4.33° (*c* 10.0, cyclohexane).

To a solution of 6.2 g (18 mmol) of 8 thus obtained in 10

ml of tetrahydrofuran (THF), 9 ml of 2.4 M phenylmagnesium chloride in THF solution was added dropwise under stirring at room temperature. The mixture was heated at reflux for 5 hr, and then hydrolyzed with a saturated aqueous ammonium chloride solution. After working up in the usual manner, distillation gave 3.1 g (71%) of methyl-α-naphthylphenylsilane (1a), bp 157° (2.5 mm), $[\alpha]_D^{20}$ +5.45° (*c* 15.7, cyclohexane), (ref.[2]: optically pure (*R*)-1a, $[\alpha]_D$ +35.0° (*c* 15.6, cyclohexane)).

2. Reaction of α-naphthylphenylsilane (5b). The hydrosilylation with 5b was carried out in the same manner as the procedure for 5a, except that the adduct, alkoxy-α-naphthylphenylsilane, was treated with methylmagnesium bromide in ether solution.

REFERENCES AND NOTES

1. A preliminary communication has appeared in Tetrahedron Lett., 331 (1974).
2. L. H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, Inc., New York, N. Y., (1965).
3. R. J. P. Corriu and J. P. Masse, Tetrahedron Lett., 5197 (1968).
4. R. J. P. Corriu and G. F. Lanneau, Tetrahedron Lett., 2711 (1971); *idem*, J. Organometal. Chem., 64, 63 (1974).
5. A. Holt, A. W. P. Jarvie, and G. J. Jervis, J. Chem. Soc. Perkin II, 114 (1973).
6. J. F. Klebe and H. Finkbeiner, J. Amer. Chem. Soc., 90, 7255 (1968).
7. a) K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 54, C45 (1973). b) T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 4405 (1974). c) *Idem, ibid.*, 3 (1975).
8. a) I. Ojima, T. Kogure, and Y. Nagai, Chem. Lett., 541 (1973);

I. Ojima and Y. Nagai, Chem. Lett., 223 (1974); I. Ojima, T. Kogure, and Y. Nagai, Tetrahedron Lett., 1889 (1974). b) W. Dumont, J.-C. Poulin, T.-P. Dang, and H. B. Kagan, J. Amer. Chem. Soc., 95, 8295 (1973).

9. a) R. J. P. Corriu and J. J. E. Moreau, Tetrahedron Lett., 4469 (1973). b) *Idem*, J. Organometal. Chem., 64, C51 (1974).
10. T.-P. Dang and H. B. Kagan, Chem. Commun., 481 (1971); *idem*, J. Amer. Chem. Soc., 94, 6429 (1972).
11. Ojima and coworkers[12] and Corriu *et al.*[13] have reported that chlorotris(triphenylphosphine)rhodium(I) is very effective catalyst for the hydrosilylation of carbonyl compounds, providing a selective route to synthesize bifunctional alkoxysilanes.
12. I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, Bull. Chem. Soc. Japan, 45, 3506 (1972).
13. R. J. P. Corriu and J. J. E. Moreau, Chem. Commun., 38 (1973).
14. It should be mentioned that optically active bifunctional alkoxysilanes might be configurationally labile under the reaction conditions, because we have a problem in obtaining reproducible data of the optical activity of these compounds.
15. L. H. Sommer, P. G. Rodewald, and G. A. Parker, Tetrahedron Lett., 821 (1962).
16. C. Eaborn, D. J. Tune, and D. R. M. Walton, J. Chem. Soc. Dalton, 2255 (1973).
17. However, the possibility still remains that the diastereomeric diorganosilylhydridorhodium moiety is in a dynamic equilibrium *via* diorganosilylenedihydridorhodium intermediates favoring a (*S*)-diorganosilyl side.
18. a) K. Ohno and J. Tsuji, J. Amer. Chem. Soc., 90, 99 (1968), and their preceding papers cited therein. b) M. C. Baird, C. T. Nyman, and G. Wilkinson, J. Chem. Soc. A, 348 (1968).

CONCLUSION

The most extensive review on "Asymmetric Organic Reactions" done by Morrison and Mosher in 1971 could not give a proper and comprehensive coverage of catalytic asymmetric reactions. Since then, an increasing attention to "asymmetric catalysis" has been appraised to be of use for a potential method for obtaining chiral molecules on the one hand, and of significant help in the recognition of "coordination catalysis" exhibited by a variety of transition metal complexes on the other.

The catalytic asymmetric hydrosilylation presented in this thesis does provide, in the author's opinion, an attractive approach to these goals.

No less exciting is the value of a well designed and executed asymmetric catalysis!

LIST OF PUBLICATIONS

Chapter 1 K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 28, C37 (1971).

Chapter 2 K. Yamamoto, T. Hayashi, and M. Kumada, J. Amer. Chem. Soc., 93, 5301 (1971).

Chapter 3 K. Yamamoto, T. Hayashi, Y. Uramoto, R. Ito, and M. Kumada, to be published.

Chapter 4 T. Hayashi, K. Yamamoto, and M. Kumada, to be published.

Chapter 5 K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 46, C65 (1972).

Chapter 6 K. Yamamoto, T. Hayashi, and M. Kumada, J. Organometal. Chem., 54, C45 (1973).

Chapter 7 T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 4405 (1974).

Chapter 8 T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 3 (1975).

Chapter 9 T. Hayashi, K. Yamamoto, and M. Kumada, Tetrahedron Lett., 331 (1974).

Other Publications not Included in This Thesis

Determination of Enantiomeric Purity of 1-Phenylalkanols Using a Chiral NMR Shift Reagent: K. Yamamoto, T. Hayashi, and M. Kumada, Bull. Chem. Soc. Japan, 47, 1555 (1974).